A DETERMINATION OF THE FREE ENERGY OF FORMATION OF THE MANGANOUS ION FROM THERMAL DATA[1]

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In the original paper an account was given of an attempt to obtain the standard potential of manganese from thermal measurements. Several heats of reaction were determined and the results combined with data supplied by other workers, a choice being presented in several instances. The National Bureau of Standards compilation of selected thermodynamic data which appeared subsequently showed that some of the values chosen originally were not the best available. The figures selected by the Bureau of Standards which differed from those quoted in the paper are:

	Kilocals./mole
Heat of formation and dilution of HCl (ΔH_5)	−78.44
Heat of dilution of HCl ($-\Delta H_8$)	−1.61
Free energy of chloride ion	−31.35
Free energy of water (1)	−56.69
Heat of dilution of H_2SO_4 ($-\Delta H_{13}$)	−5.3

The adoption of these figures results in a value for the free energy of formation of the manganous ion which is 0.33 kilocalories more negative than that previously calculated. The specific values derived are listed below.

Heat of formation of $MnCl_2 \cdot 4H_2O$ (ΔH_7)	−403.98
Free energy of $MnCl_2 \cdot 4H_2O$	−340.52
Free energy of manganous ion	−54.89
Heat of formation of manganous ion—HCl method (ΔH_{10})	−53.18
Heat of formation of manganous ion—H_2SO_4 method (ΔH_{15})	−52.6
Entropy of manganous ion (approximate value only)	−17.9 units
Standard potential of Mn based on the value $\bar{G}^{\circ}_{Mn^{++}} = -54.89$	−1.190 volts

The calculation of $\bar{G}^{\circ}_{Mn^{++}}$ from the solubility product of $Mn(OH)_2$ is unchanged at −54.9 kilocals./mole.

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THE ELECTRICAL CONDUCTIVITY OF LEAD DIOXIDE[1]

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ABSTRACT

The electrical conductivity of lead dioxide has been measured for dense samples prepared by the electrolysis of lead perchlorate and other lead salts and for porous samples prepared from storage battery oxides and from pressed powder. The specific resistance of the dense samples is of the order of 2×10^{-4} ohm-cm. That of the battery material is 74×10^{-4} ohm-cm. The resistance increases with temperature by about 0.2 per cent per degree at room temperature.

A mechanism for conduction is proposed which assumes that lead dioxide is not of exact stoichiometric composition, but contains an excess of lead, which is considered to be dissociated into tetravalent lead ions and free electrons. The conductivity is due to the latter. Hall effect measurements have been made from which the density of carriers is shown to be about 4.4×10^{20}/cm.^{3} or 1.8×10^{-2} carriers per molecule.

INTRODUCTION

Lead dioxide, commonly called the peroxide, is widely used in a porous form as the active material of the positive plate of the familiar lead-acid storage battery. The same substance in a much more dense form is used in the lead-perchloric acid battery (1). One of the properties of this material which is important for its use in batteries is the good electrical conductivity which it exhibits. It has long been known as a good conductor, but as far as the author has been able to determine very little quantitative data has been published in this country and almost nothing has been known of the nature of the conduction. This paper will describe experiments in which the conductivity and its temperature coefficient have been measured for samples of PbO_2 prepared in various ways. A mechanism for the conduction is proposed, based on measurements of the Hall effect.

EXPERIMENTAL

Preparation of specimens

The special forming mold shown in Fig. 1 was made from sheet methyl methacrylate. A rectangular recess, 8 x 0.6 x 0.12 cm., was filled with a standard commercial storage battery positive paste. A strip of lead foil with perforations to match those in the mold cover was then applied to the paste to serve as a "grid" during the formation process. A sheet of filter paper was placed over the lead foil and the perforated cover secured in place with plastic screws. The entire assembly was immersed in sulfuric acid (sp. gr. 1.100). With sheet lead as cathode, the paste mixture was made anode and the material was "formed," i.e., converted to PbO_2, by making it anode for a period of about one week, after which the PbO_2 was almost black in color. The grid and cover plate were removed and the

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sample was thoroughly washed in distilled water and dried in a desiccator. The electrical conductivity of the sample was then measured as described later. Samples prepared in this way are believed to be typical of battery positive active material.

It is recognized that the physical and chemical properties of battery active material are dependent on many factors, including the temperature and other conditions of formation (2). Undoubtedly, these factors also alter

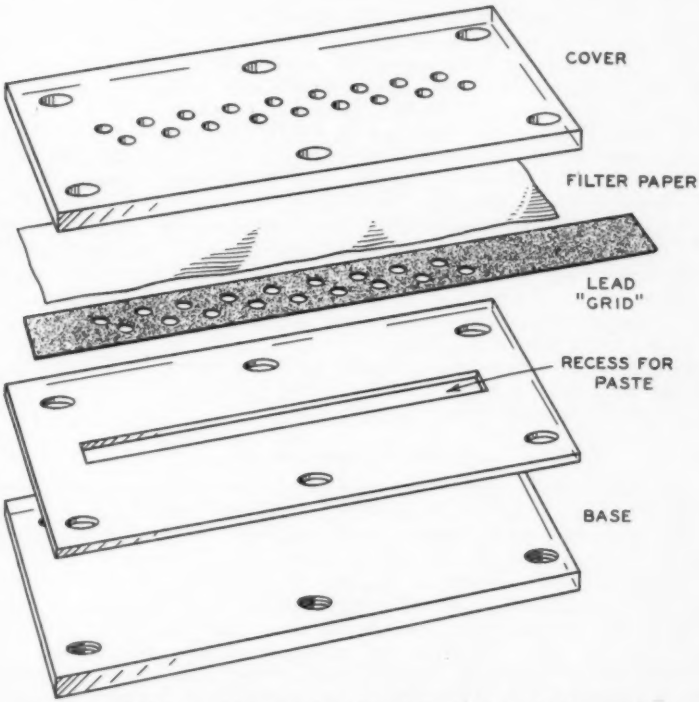

FIG. 1. Mold for making samples of lead dioxide from battery paste

the electrical properties of the final material. Because of the complexity of these factors and the indeterminate detailed geometry of such materials, it seemed advisable to choose other forms of lead dioxide for studies of its fundamental properties.

For this reason, dense samples were prepared by the electrolysis of a slightly acid lead perchlorate solution, using a platinum anode (4 x 4 cm.) and a lead cathode. The electrolyte was made by nearly saturating a 30 per cent solution of perchloric acid with solid litharge, PbO. During electrolysis, PbO_2 was deposited as a dense film on the anode and lead was plated out on the cathode. This resulted in a net loss of PbO from the

electrolyte; consequently, the solution was periodically replenished by additions of litharge. A current density of about 0.2 amp./dm.^{2} was found to be satisfactory. At this rate, a thickness of 0.23 mm. of PbO_2 was deposited per day. If the layer was allowed to become thicker than 0.5 mm. it buckled and cracked away from the basis metal. Therefore, when the film was 0.1 to 0.2 mm. thick, it was carefully removed from the platinum, using a razor blade or thin spatula. The material was very fragile and required great care in handling. A nickel wire was cemented to one edge of the thin sheet of PbO_2 with a conducting cement (silver powder in cellulose nitrate cement). With the wire as electrical contact and mechanical support, the sheet was suspended in the bath and electrolysis continued until the sample was about 2 mm. thick. Since PbO_2 was deposited on both sides of the thin sheet, buckling was avoided. The final plate of PbO_2, 4 x 3 x 0.2 cm., was then sawed into strips 4 x 0.4 x 0.2 cm. It was necessary to use a diamond saw because the material is extremely hard and brittle. The strips were lapped with alundum powder in water to provide flat, parallel faces.

Moderately thick layers of PbO_2 were prepared also by electrolysis of lead nitrate, lead acetate, and lead sulfamate solutions. All the electrolytic films were dense, hard, brittle, and almost black in color with a definite metallic luster. Those made from acetate and nitrate solutions cracked and peeled so badly that samples large enough for convenient measurement of conductivity were not obtained.

Porous samples were also prepared by compressing C.P. lead dioxide powder into discs, using a pressure of 14 kg./mm.^{2} (10 tons/in.^{2}). The discs were dark brown with a metallic sheen.

Resistivity measurements

The specific resistance of the various samples was measured using a method which eliminates errors due to contact resistance between the sample and the current leads. Four connections were made along the length of each sample. The outer two served as current leads and the inner two as voltage probes. Various measured currents were passed through the specimens and the potential difference between the voltage probes was determined with a potentiometer. The current density usually employed was about 1.3 amp./cm.^{2}; however, measurements were made over the range 0.5–5 amp./cm.^{2} The specific resistance of the sample was then calculated from the current, the voltage drop, and the dimensions of the test piece. Contacts to the sample were made in one of three ways. Copper wires were cemented to the PbO_2 with conducting cement, thin strips of silver foil were pressed directly against the specimen or against areas on its surface onto which a thin layer of gold had been evaporated.

In every case the resistance was found to be ohmic, i.e., it was independent of the direction, magnitude and duration of the current within the limits of the experiment. Table I gives the results of a number of measurements.

Temperature coefficient of resistivity

The resistance of samples of dense PbO_2 made from perchlorate solution was measured at various temperatures in the range $-195°$ to $+100°$C.

One difficulty encountered was the uncontrolled and irreversible variation of the resistance of a specimen during repeated temperature cycles. These variations, while relatively small, were large enough compared to the reversible changes due to temperature to reduce the accuracy of the determination of the temperature coefficient of resistivity. However, an approximate curve of resistivity as a function of temperature can be obtained as shown in Fig. 2. From these data it appears that the temperature coefficient in the range -190 to -90°C. is about 0.07 per cent of the room temperature value per degree and that it rises to about 0.2 per cent per degree at 60°C.

Hall effect measurements

In 1879 Hall (3) discovered that a potential difference is produced transversely across a strip of metal carrying a current when placed in a magnetic field normal to the plane of the strip. From measurements of the sign and magnitude of this potential, it is possible to gain important fundamental information as to the mechanism of conduction in metals and semiconductors. For a further discussion of the Hall effect and its application to studies of this type, the reader is referred to a paper by G. L. Pearson,

TABLE 1. *Resistivity of various samples of PbO_2 at room temperature*

	ohm-cm.
Storage battery positive active material—46 per cent porosity	74×10^{-4}
Pressed powder—32 per cent porosity	142×10^{-4}
Electrolysed from lead perchlorate—dense	0.94×10^{-4} to 4.05×10^{-4}
Electrolysed from lead sulfamate—dense	12×10^{-4}

"The Physics of Electronic Semi-conductors," (4). It can be shown that the density of current carriers can be calculated from the following equation:

$$R = \frac{10^8 V\, t}{IH}$$

where V is the transverse potential developed in the magnetic field, H the intensity of the field in gausses, t the thickness of the sample in centimeters, and I the current in amperes. R is the Hall coefficient in cubic centimeters per coulomb. From the value of the electronic charge in coulombs and the experimental value of R, the density of current carriers can be calculated, assuming that each carries a unit electronic charge. The sign of the charge of the carrier can be determined from the sign of the Hall coefficient. It is also possible to calculate the mobility of the carriers if the resistivity of the sample is known. Table II lists the results obtained on two samples of PbO_2 from perchlorate solution.

The negative sign of the Hall coefficient indicates that the carriers have a negative sign, and their high mobility indicates that these carriers are electrons rather than negative ions. The sign of the thermoelectric power was also such as to indicate a negative charge on the carriers.

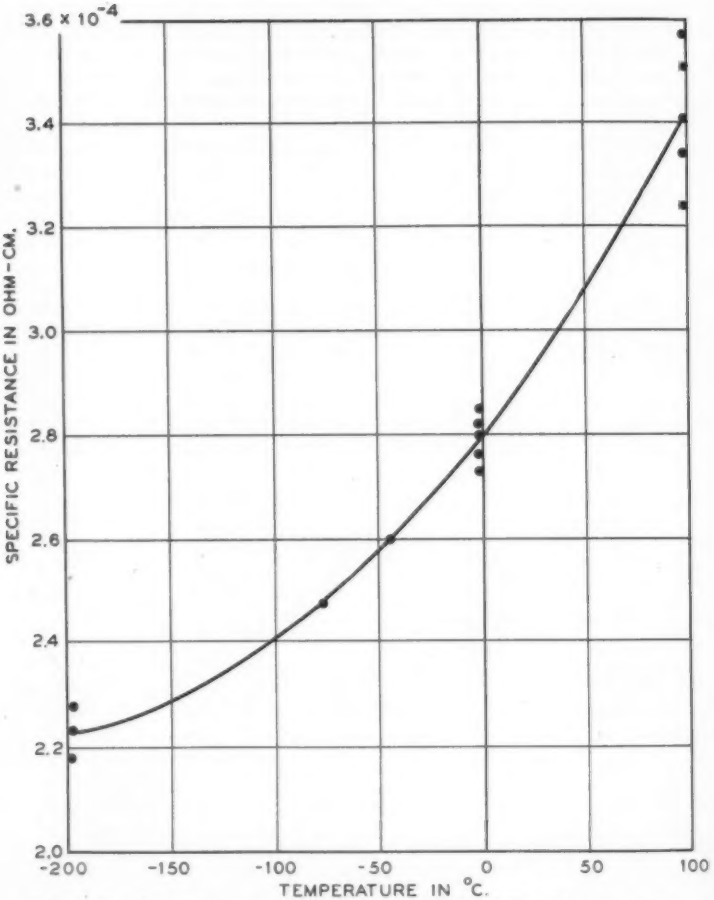

FIG. 2. Specific resistance of lead dioxide as a function of temperature

TABLE II. *Hall effect data on PbO_2 at room temperature*

	Sample 1	Sample 2
Temperature, °K	295	295
R, Hall coefficient, cm.³/coulomb	-3.7×10^{-2}	-1.7×10^{-2}
Density of carriers, cm.$^{-3}$	2.0×10^{20}	4.4×10^{20}
Density of PbO_2 (estimated) gms./cm.³	9.55	9.55
Carriers per molecule	0.83×10^{-2}	1.8×10^{-2}
Specific conductance, ohm^{-1} cm.$^{-1}$	not meas.	1.06×10^{4}
Mobility of carriers, cm./sec./volt/cm.	—	150

X-ray structure data

X-ray diffraction patterns were made on two samples of PbO_2. One sample was dense material made electrolytically from sulfamate solution; the other was the C.P. lead dioxide powder used for making the pressed discs. The structure and the cell constants were identical within experimental error for the two samples. The structure found is the normal tetragonal PbO_2, similar to the rutile form of TiO_2, and is illustrated in Fig. 3. The cell constants observed were $a_0 = 4.950 \pm 0.005$ Å and $c_0 = 3.36 \pm 0.02$ Å.

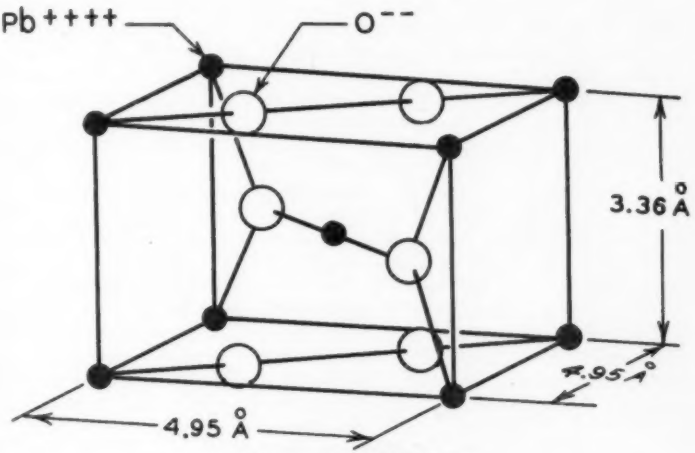

FIG. 3. Unit cell PbO_2

DISCUSSION OF RESULTS

The data obtained in this study show that solid lead dioxide has a specific resistance at room temperature of the order of 1 to 3 $\times 10^{-4}$ ohm-cm. Thus, PbO_2 is more conducting than graphite (8×10^{-4} ohm-cm.). The poorly conducting metals such as mercury and bismuth have resistivities about equal to that of lead dioxide. No other chemical compound yet measured has as low a resistivity. Cuprous oxide, generally considered to be a fairly good conductor, is higher in specific resistance by a factor of at least 10^8 at room temperature.

It is interesting to compare the resistivities of some of the components of the storage battery. We have seen that the positive active material when fully charged has a specific resistance of about 70 $\times 10^{-4}$ ohm-cm. as measured on a porous sample. A dense sample of pure lead has a value of about 0.22 $\times 10^{-4}$ ohm-cm., while that of sulfuric acid, sp. gr. 1.200, is of the order of 1.2 ohm-cm., nearly 200 times that of the positive paste.

W. H. Palmaer (5) measured the electrical properties of lead dioxide made by electrolysis of dilute lead nitrate solution. He found a resistivity of 0.92 $\times 10^{-4}$ to 0.97 $\times 10^{-4}$ ohm-cm. with a positive temperature coefficient

of 0.06 per cent per degree in the range 22–84°C. The present study is in approximate agreement with these findings. Palmaer determined the purity of his samples by a method of chemical analysis in which the PbO_2 was used to oxidize oxalic acid. These determinations indicated that his samples contained 99.1 per cent PbO_2, but gave no information as to the nature of the 0.9 per cent impurity.

In order to understand the means by which lead dioxide conducts electricity, it will be necessary to look briefly into the process of electrical conduction in the light of the modern theory of solids. For a further description, the reader is referred to the paper by Pearson (4) and to the references given there. Solids conduct electricity at room temperature chiefly by means of the motion of electrons free to move throughout the crystal lattice. The amount of the conductivity will depend on the number of such free or "conduction" electrons and on their mobility. Metals are characterized by a very large number of conduction electrons, of the order of one for each atom. In general, the resistance of metals is increased by increased temperature or by the presence of impurities. This is because the disorder introduced into the lattice by foreign atoms or by thermal vibration interferes with the motion of the electrons, reducing their mobility. Insulators, on the other hand, do not conduct electricity because the number of free electrons which they contain is vanishingly small. There is an intermediate class of materials, called semi-conductors, such as zinc oxide, cuprous oxide, and many others, which have moderate conductivity at room temperature. In general, these materials show increased conductivity with increased temperature and with the presence of impurity atoms. In many cases the "impurity" may be merely a slight excess over the stoichiometric amount of one of the atoms normally present in the compound. In the case of cuprous oxide, for example, the impurity is a slight excess of oxygen. The chemist may prefer to view this as a very dilute solid solution of cupric oxide in cuprous oxide. In any case, the number of current carriers, which may be electrons or positively charged "electron holes," is increased by a rise in temperature or by the addition of impurity atoms. Each impurity atom is a potential source of one or more carriers and the number of free carriers will usually increase with temperature.

Lead dioxide has characteristics which more nearly approach those of metals than those of semi-conductors. Its conductivity is much higher than that of most semi-conductors and decreases with temperature. The Hall effect measurements given in Table II indicate that there is a very large number of free carriers, in this case electrons, available for conduction. It may be assumed that these arise because of a departure from stoichiometric composition, in the direction of an excess of lead.

In this case there would be a deficit of at least two oxygen atoms for each four free electrons or, alternatively, there would be at least one additional lead atom which is dissociated into a tetravalent lead ion and four electrons. If dissociation is incomplete, the required departure from stoichiometry would have to be greater. Taking the value of 1.8×10^{-2} carriers per molecule from Table II, the composition of the sample would be $PbO_{1.991}$. Chemically, this is equivalent to $PbO_{2.000}$ with 0.9 mol. per cent of PbO in solid solution. It may be coincidence, but such a sample should give the analytical result, namely 99.1 per cent PbO_2, reported by Palmaer for a sample of the same resistivity.

The two values of the Hall coefficient in Table II indicate that the number of carriers, and presumably the exact amount of departure from stoichiometry, differs from one sample to another and probably accounts in large part for the variation in resistivity from sample to sample. The fact that resistivity continues to decrease with decreasing temperature down to −195°C. indicates that the number of conduction electrons is probably nearly independent of temperature, the resistance change being due to changes in their mean free path.

From the structure it appears probable that the deficit in oxygen results in the presence of interstitial Pb^{++++} ions which could exist with only minor distortion of the lattice. LeBlanc and Eberius (6) made X-ray diffraction studies of PbO_2 in which they reported that oxygen could be removed from PbO_2 by treating at temperatures above 140°C. in vacuum, and that no phase change took place down to a composition of $PbO_{1.66}$. The diffraction patterns published in their paper indicate a progressive increase in the lattice constants with the removal of oxygen. This is consistent with the presence of the excess lead in interstitial positions in the lattice.

Samples of PbO_2 prepared in different ways all had high conductivities differing by not more than a factor of 150. No special heat treatment was required to produce conductivity. This suggests that the thermodynamically stable form of lead dioxide at room temperature departs appreciably from its nominal composition, unlike, for example, Cu_2O which must be heated in oxygen and quenched to induce reasonably good conductivity. If the conclusions of LeBlanc and Eberius are correct, it should be possible to make PbO_2 even more conducting by heating in vacuo to temperatures above 140°C. If experimental means could be found for increasing the oxygen content of a sample of PbO_2, its conductivity should be decreased as a result.

ACKNOWLEDGEMENTS

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Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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ELECTROLYTIC REDUCTION OF AQUEOUS TUNGSTATE SOLUTIONS[1]

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ABSTRACT

A "catalytic reduction" theory is proposed to explain the electrolytic reduction of aqueous tungstate solutions in the presence of codepositing metals such as iron, nickel, and cobalt. Two cathode reactions are suggested as being essential to the reduction process:

$$M^{++} + 2e \rightarrow M \qquad (A)$$

$$WO_4^{=} + 8H^{+} + 6e \xrightarrow{(M)} W + 4H_2O \qquad (B)$$

Reaction A proceeds until the cathode is covered with a thin deposit of metal, M, which then acts as a catalyst for reaction B. When this metal catalyst is covered with a layer of tungsten reaction B stops and reaction A again proceeds to give a new catalyst surface; thus alternate layers of metal (Ni, Co, or Fe) and tungsten are deposited on the cathode. Evidence for this postulated mechanism is based in part on polarographic studies, cathode potential measurements, and the laminated structure of the cathode deposits.

INTRODUCTION

It is well known that the reduction products obtained at the cathode during electrolysis of aqueous tungstate solutions depend on such conditions as the pH of the electrolyte, the nature of the cathode material, cathode current density, and bath temperature. In general it can be said that *pure* aqueous neutral or alkaline tungstate solutions are not reduced on electrolysis, whereas acid solutions are readily reduced. Electrolytic reductions of W^{VI} to W^{V}, W^{IV}, W^{III}, and W^{0}, as well as intermediate states, have been reported. Recently, greatest interest has been shown in the reduction of acid as well as alkaline $WO_4^{=}$ solutions in the presence of Ni^{++}, Co^{++}, Fe^{++}, or Fe^{+++}, where the reduction products are so called alloys of tungsten.

The most common readily available water soluble W^{VI} compound is hydrated sodium tungstate, $Na_2WO_4 \cdot 2H_2O$. This compound, or the corresponding potassium compound, is easily prepared from H_2WO_4 or its anhydride WO_3 by treatment with hot aqueous sodium (or potassium) hydroxide or carbonate solution. When a strong acid, as HCl, HNO_3, or H_2SO_4, is added to an aqueous tungstate solution, insoluble H_2WO_4 or one of its hydrates is formed; however the addition of such acids as H_3PO_4, HCOOH, CH_3COOH, or $H_2C_2O_4$ does not give an immediate precipitate. It is interesting to note that on the addition of an excess of concentrated HCl to a $WO_4^{=}$ solution the precipitate redissolves, possibly due to the formation of soluble WO_2Cl_2 or $WO_2Cl_3^{-}$. Simple tungsten compounds

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as the chloride, WCl_6, or the bromide can be prepared without great difficulty but these compounds readily undergo hydrolysis and are not suitable for use in aqueous solutions. Thus it can be seen that reduction studies in aqueous media usually involve solutions of the tungstates.

The purpose of this paper is to review some of the more pertinent published information dealing with cathode products obtained during the electrolysis of aqueous tungstate solutions and to consider possible mechanisms of the reduction processes, particularly the reduction of W^{VI} compounds to metallic tungsten in the presence of certain cations.

Some previous work

Reduction of W^{VI} to W^{V}, W^{IV} and W^{III}

There are numerous published reports of the cathodic reduction of acid tungstate solutions with reduction products that seem to be fairly definite. Collenberg and Nilsson (1) reported that a strong oxalic acid solution of K_2WO_4 was reduced to the deep blue W^{V} at lead or tin cathodes if the temperature of the solution was 70°C. or above. Collenberg and Backer (2) found that solutions of alkali tungstates in concentrated HCl were reduced quantitativly to W^{V} at a platinum cathode. They also noted that solutions of sodium tungstate in concentrated HCl were reduced to W^{III} at cathodes of mercury, tin, or lead when the temperature was 16°C. or above. The electrolytic reduction of a solution of WO_3 in HF or HCl to $WO_2 \cdot 2H_2O$ or $W(OH)_4$ was reported by Bernhardi-Grisson (3).

Reduction of W^{VI} to W^{0} with no codepositing metal

Feree (4) was one of the first to report the electrolytic reduction of an aqueous solution of a tungsten compound to metallic tungsten. He obtained tungsten by the electrolysis of a solution of WO_3 in hydrofluoric acid using a mercury cathode. Jackson, Russell, and Merrill (5) used the same type of solution and found that 2 to 20 per cent of the W^{VI} present was reduced to the metal at a mercury cathode. In 1931 Fink and Jones (6) reported the electrolytic reduction of alkaline $WO_4^{=}$ solutions to metallic tungsten with only a small amount of reduction and very low current yield. Yntema (7) reported the reduction of a citric acid-tungstate solution with only a small amount of metal obtained. Recently a patent was granted to Harford (8) for the electrodeposition of tungsten from an aqueous bath containing a tungsten salt and an alkyl hydrocarbon polyamine with a bath pH greater than seven.

Reduction of W^{VI} to W^{0} in the presence of certain cations

Most of the recent work on the electrolytic reduction of aqueous tungstates has dealt with solutions containing metallic ions which are reduced simultaneously with the W^{VI} to give alloys of tungsten as the cathode products. Fink and Jones (6) reported that alloys of Ni-W and Fe-W were deposited from the carbonate-tungstate bath when nickel and iron anodes were used. In 1932 Fink (9) was granted a patent on the use of nickel salts (and certain other compounds) as depolarizing agents in the carbonate-tungstate bath; this was claimed to give a "substantially pure" tungsten deposit. It was later suggested (10) that the reduction of W^{VI} to the

metal in the carbonate-tungstate bath appeared to be due to the presence of small amounts of iron present as an impurity in the materials used; this was also found to be true for the phosphate bath (11) and the citric acid bath (7). Other work (12) reported that Ni^{++}, Co^{++}, Fe^{++} and Fe^{+++} definitely aid in the cathodic reduction of tungstates in the carbonate bath, in acid baths (13, 14, 15), and in other types of alkaline baths (16, 17, 18). The patents of Armstrong and Menefee (19) also mention certain of these metals as codepositing with tungsten.

EXPERIMENTAL

Various theories have been offered to explain the effect of Ni^{++}, Co^{++}, Fe^{++}, and Fe^{+++} on the electrolytic reduction of aqueous tungstate solutions. Complex formation, reduction by atomic (active, or nascent) hydrogen, and catalytic action have been suggested. The experimental work carried out in an attempt to find evidence which might lead to a reasonable explanation of these effects was divided into two parts: (a) polarographic studies, and (b) cathode potential measurements.

Polarographic studies

The polarographic investigation of tungstate solutions was undertaken mainly to determine if there was evidence of complex formation between the codepositing metals and tungstate ion. It was hoped that tungstate would have a different effect on the polarographic waves of codepositing metals than it did on the waves of metals such as zinc, manganese, and cadmium which apparently do not codeposit with tungsten. It was realized that since only very dilute solutions of the reducible substances can be used in polarographic studies the extrapolation of the results to actual plating bath conditions would be difficult or even impossible.

Very little work has been done on the polarography of tungsten compounds. Stakelberg and coworkers (20) found that although a soluble tungstate did not produce a wave in neutral or alkaline solutions, it did give a well defined wave in ten normal HCl with a half wave potential of -0.42 v. measured against the standard calomel cell. Souchay (21) has investigated tungsten poly- and heteropoly-acids, such as silicotungstates, phosphotungstates, metatungstates, and borotungstates in which polarography was one of the methods used. Curves for the polytungstates were somewhat irregular but apparently reproducible. The pH was generally on the acid side and no wave was found for orthotungstate in the potential range considered.

Procedure

The methods and theory of polarography are quite well known (22) and need not be described in detail here. In this work a Sargent Heyrovsky Polarograph, Model XI, was used. The glass polarographic cell was so designed that nitrogen could be bubbled into the solution to remove oxygen from the system. The bridge voltage used was 2.5 v. The supporting electrolyte was 0.1 molar LiCl. The metal sulfate solutions were 10^{-3} molar and the sodium tungstate solution was 2×10^{-3} molar. To suppress the maximum a solution of 1 per cent methyl cellulose and 0.1 per cent ammonium eosin was used. The polarograms obtained have the potential

as the abscissa and the current as the ordinate. All potentials were measured against the saturated calomel cell.

Results

The nickel wave is shown in Fig. 1 and the nickel-tungstate wave is given in Fig. 2. It can be seen that these curves are very much alike. At a sensitivity of $\frac{1}{20}$ the nickel wave had a half-wave potential of -1.06 v., a maximum current of 4.28 microamperes, and a break-off potential of -2.02 v. The nickel wave in the presence of WO_4^{--} had a half-wave potential of -1.05 v., a maximum current of 4.22 micro-amperes, and a break-off

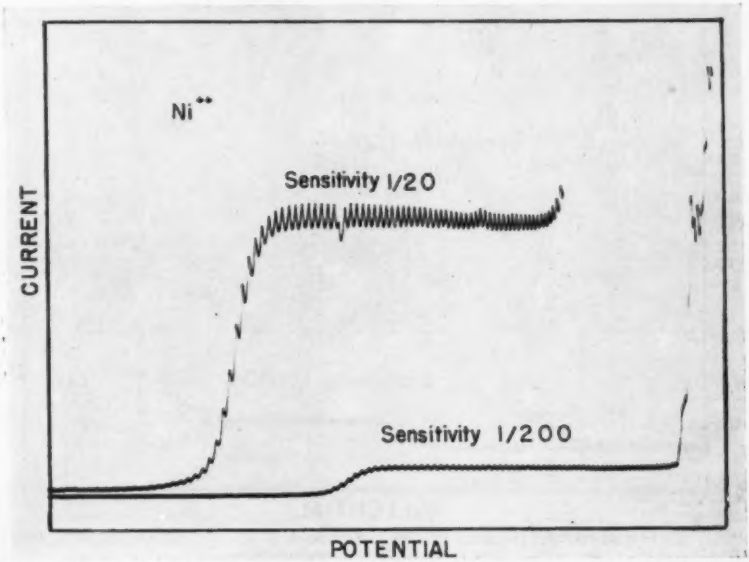

FIG. 1. The nickel polarogram, with 0.1 molar LiCl, 10^{-3} molar $NiSO_4$, and 2 drops of suppressor

potential of -1.67 v. At a sensitivity of $\frac{1}{20}$ and in the presence of tungstate ion the current increased abruptly at a potential of -1.59 to -1.67 v., and this part of the curve is very steep. At a sensitivity of $\frac{1}{200}$ this same abrupt increase was noted but the slope is small. When a potential of -1.80 v. was reached the current again increased abruptly going to a very high value. This same behavior was observed with cobalt in the presence of tungstate but not with zinc, cadmium, and manganese. It was found further that, at the conditions used, the half-wave potentials for nickel, cobalt, zinc, cadmium, and manganese cations were about the same in the presence and in the absence of tungstate ion and therefore complex formation is not indicated.

Cathode potentials

The measurement of cathode potentials during electrolysis is difficult and the results obtained are not very reproducible. The "direct method" and the "commutator method" have been used frequently; the former method seemed most feasible for this work. It was expected that cathode potential measurements of tungstate solutions in the presence and absence of codepositing metals would give information about the reduction process.

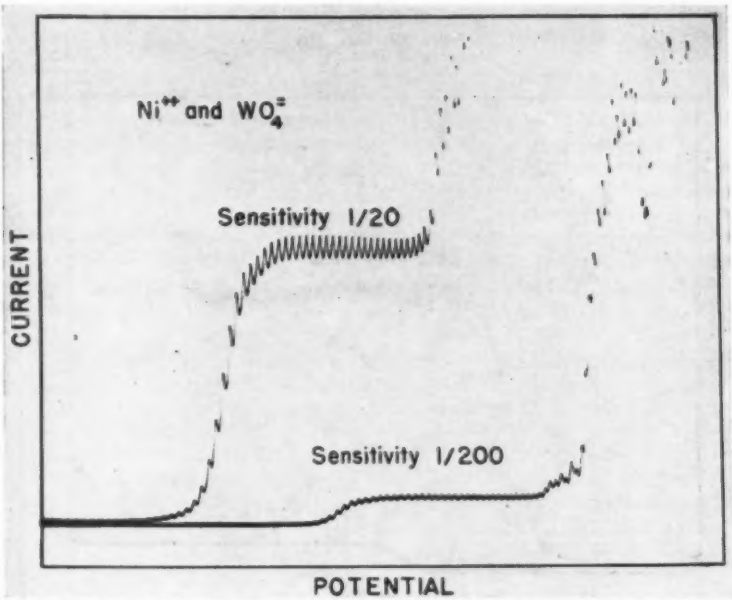

FIG. 2. The nickel polarogram in the presence of 2×10^{-3} molar Na_2WO_4, with 0.1 molar LiCl, 10^{-3} molar $NiSO_4$, and 2 drops suppressor.

Procedure

A saturated calomel cell was used as the reference electrode. The end of the KCl salt bridge was drawn out to a tip of somewhat less than one millimeter diameter and was loosely plugged with filter paper pulp to minimize the flow of the bridge solution. The cathodes were polished and cleaned and then coated on one side with glyptal or asphaltum. The 3 x 3 cm. copper cathode and the platinum anode of the same size were supported in a specially designed lucite cell which kept the electrodes in place and allowed the electrolyte to circulate freely. This electrolysis cell was placed in a beaker containing the electrolyte which was then set in a water bath to maintain a temperature of about 25°C. The tip of the salt bridge from the calomel cell was then placed against the cathode metal at about its center. Direct current was supplied by a variable voltage

rectifier of our own design. Cell potentials at various time intervals during electrolysis were measured on a student type Leeds and Northrup potentiometer.

Two different baths of the ammoniacal citrate type (17) were used; one of these contained Ni^{++} and $WO_4^{=}$ and the other contained Ni^{++} only. Both of these baths on electrolysis gave a metal deposit on a copper cathode; thus it was assumed that in a short time the cathode surface was characteristic of the bath and that the cathode potential measured was the potential between the bath and the surface that it deposited on the cathode. The composition of the two baths used is given in Table I.

TABLE 1. *Composition of the baths used for cathode potential studies*

Compound	Bath I (nickel)	Bath II (nickel-tungstate)
$NiSO_4 \cdot 6H_2O$	20 g./l.	20 g./l.
Citric acid	66 g./l.	66 g./l.
$Na_2WO_4 \cdot 2H_2O$	none	50 g./l.
Ammonia	to pH 8	to pH 8

TABLE II. *Cathode potentials in the ammoniacal citrate nickel bath and nickel-tungstate bath during electrolysis at different current densities. Temp. 25°C.*

Cathode current density	Cathode potential at 20 minutes	
	Bath I (Ni)	Bath II (Ni-W)
amp./dm.²		
1.28	−1.07	−0.90
2.55	−1.08	−0.92
5.10	−1.05	−0.97
10.2	−1.14	−1.05
15.3	−1.15	−1.08
25.5	−1.2	−1.12

Results

It was found, as expected, that the cathode potentials were not exactly reproducible and that they changed, particularly during the first part of the run; however after about twenty minutes of electrolysis the potentials seemed to remain fairly constant and were fairly reproducible. A comparison of the cathode potentials determined in the two baths after 20 minutes electrolysis with various cathode current densities is given in Table II.

Temperature of the bath was found to have an effect on cathode potentials. An increase of bath temperature decreased the cathode potential and, in general, this effect was somewhat greater with the nickel-tungstate bath than with the nickel bath.

DISCUSSION

It is remarkable that, up to the present time, aqueous W^{VI} solutions have been reduced to the metal in appreciable amounts only in the presence of

certain metal ions which are at the same time also reduced to the metallic state. The presence of these codepositing metals seems essential to the reduction process that is taking place at the cathode. The fact that various types of electrolytic baths can be used suggests that there is a single fundamental reaction which makes this type of reduction possible.

Glazunov and Jolkin (23) have made some interesting observations regarding the cathodic reduction of aqueous tungstate solutions. They found that a very thin film of tungsten was deposited on a copper cathode from a concentrated aqueous carbonate-tungstate solution electrolyzed at a high temperature (115°C.) and a high current density. After one-half hour of electrolysis the deposition of tungsten stopped and the deposited tungsten began to redissolve. They suggest that this is not due to a change in the electrolyte since more deposits of tungsten can be obtained on new copper cathodes. The primary process according to them is the deposition of a lower oxide on the cathode which is then reduced to the metal by atomic hydrogen. This reaction is soon stopped by the accumulation of tungsten ions of higher valence which react with the deposited metal. In a subsequent article Glazunov (24) explained the thin deposit of tungsten metal on the cathode by assuming that the reaction

$$W + W^{+3} = 2W^{+2}, \text{ or } W + 2W^{+6} = 3W^{+4},$$

is greater than the velocity of the reduction to metallic tungsten.

The reduction of $WO_4^{=}$, WO_3, or a lower oxide to tungsten by atomic hydrogen, although it has been proposed by others (25), is perhaps questionable. Bagotsky and Jofa (26) found that the yellow oxide of tungsten was not reduced to a lower oxide at a mercury cathode by nascent hydrogen unless the WO_3 was in actual contact with the cathode. They proposed that the reduction to the blue oxide is due to the "electron conductivity" of WO_3 and suggested the reaction

$$2WO_3 + 2H^+ + 2e \rightleftarrows W_2O_5 + H_2O$$

as a possible reduction mechanism.

The formation of a complex with tungstate and a codepositing metal has been suggested as being necessary for the cathodic reduction of aqueous tungstate solutions. Since the tungstate ion is an anion it could possibly be tied up in a complex cation and thus brought to the cathode for reduction. A complex such as $(M^{++})_x(WO_4^{=})_y$ where "x" is large enough to give the complex a positive charge is a possibility. Such a compound is doubtful as no complex has been separated from the solutions; also polarographic studies gave no evidence of complex formation because the half wave potential of a codepositing metal was not shifted by tungstate ion. This lack of evidence for complex formation does not eliminate the possibility of a small amount being present. It may mean that the equilibrium is such that only a very small amount of a complex is present.

On the basis of evidence now available it would appear that a process of catalytic reduction is the fundamental reaction taking place during the reduction of aqueous tungstate solutions. In the polarographic studies it was found that tungstate ion seemed to give a catalytic wave with most of the metallic ions used and that this effect was most pronounced with Ni^{++} and Co^{++}. Cathode potential results might also be interpreted to support

this theory because, at all current densities studied, the cathode potential in the nickel-tungstate bath was lower than the potential in the nickel bath by about the same amount. Perhaps the best evidence for the catalytic reduction theory is the laminated structure of electrodeposited tungsten alloys (18, 27). These laminations, running parallel to the basis metal, may indicate that the cathode deposit is formed in alternate layers of the codepositing metal and tungsten.

The catalytic reduction of aqueous tungstate solutions to the metal can be postulated as taking place in the following manner. The first process is the reduction reaction

$$M^{++} + 2e \rightarrow M \qquad (A)$$

where M^{++} represents an ion of a codepositing metal. When a thin layer of this metal, formed by reaction A, covers the cathode basis metal it catalyzes the reduction of tungstate ion, perhaps according to the reaction

$$WO_4^{=} + 8H^+ + 6e \xrightarrow{(M)} W + 4H_2O \qquad (B)$$

Then, when the catalyzing metal, M, is coated with a layer of metallic tungsten, reaction B stops and reaction A again proceeds to give a new catalyst surface. This is again followed by reaction B and thus alternate layers of metal and tungsten are deposited on the cathode surface. A fundamental assumption of this theory is that reaction B will not proceed unless a catalyst, M, is present. Since cathode current efficiencies in this reduction process are often very low a third reaction

$$2H^+ + 2e \rightarrow 2H \rightarrow H_2 \qquad (C)$$

occurs together with reactions A and B. The extent of reaction C depends on conditions and thus the efficiency of the reduction process which gives the metal deposits can be low or high.

Catalytic reduction can also explain the observations of Glazunov and Jolkin (23) by assuming that, at the conditions they used, copper acts to catalyze reaction B. As soon as the copper surface is coated with tungsten no further deposit is obtained because the copper is no longer effective as a catalyst and there is no codepositing ion in the solution to supply a new catalyst.

Many other metallic ions have been added to the various types of aqueous baths used for tungsten alloy production but nickel, cobalt, and iron cations seem to be the only ones that are definitely effective in promoting the reduction of tungstate to the metal. It may be that other metals catalyze the reaction but do not cause the deposition of tungsten because they have such low deposition potentials. The action of nickel, cobalt, and iron is not unexpected as these metals are well known for their catalytic activity, although future work may well show that other metals are equally effective.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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ELECTRODEPOSITION OF GAMMA MANGANESE[1]

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ABSTRACT

Procedures are given by which electrolytic manganese can consistently be deposited in the flexible gamma form rather than the usual brittle alpha form. With electrolytes containing manganese and ammonium sulfates and free of sulfur dioxide or colloidal sulfur, excellent deposits were obtained on copper cathodes at current efficiencies of 62 to 72 per cent; deposits on stainless steel cathodes were much poorer. The use of colorless ammonium sulfide for purification did not interfere with the deposition of gamma manganese, but the use of yellow ammonium sulfide, unless followed by a further purification step (presumably to remove colloidal sulfur), resulted in only slightly flexible deposits consisting of gamma manganese containing some alpha. Electrolytes containing sulfur dioxide yielded only alpha manganese. Gamma manganese deposits were used successfully as starting sheets for the deposition of alpha manganese.

INTRODUCTION

In 1925, Bradley (1) and Westgren and Phragmen (2) discovered the three allotropic forms of manganese now known as alpha, beta, and gamma. A few years later Gayler (3) and Yoshisaki (4) determined the transition points for vacuum-distilled manganese by thermal analysis and by density and dilatometric methods and obtained data showing three discontinuities, but neither of these workers recognized the significance of this. Grube (5, 6), however, observing these three discontinuities in data obtained by

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thermal analysis and magnetic susceptibility methods on vacuum-distilled metal, suggested the existence of a fourth allotropic form of manganese which is now known as delta. Sieverts and Moritz (7) supported this conclusion on the basis of changes in hydrogen solubility in vacuum-distilled manganese. Recently, Potter and Lukens (8), on the basis of their hydrogen-solubility data obtained with electrolytic manganese and the closely agreeing heat content data of Naylor (9) also obtained with electrolytic manganese, proposed the following transition points:

Alpha-beta	727°C. ± 3 (heating)
Beta-alpha	692–665°C. (cooling)
Beta-gamma	1100°C. ± 3 (heating and cooling)
Gamma-delta	1138°C. ± 3 (heating and cooling)
Delta-liquid	1245°C. ± 3 (heating and cooling)

X-ray analyses show that the alpha form of manganese has a body-centered cubic lattice with 58 atoms in the unit cell, the beta form has a body-centered cubic structure with 20 atoms in the unit cell, and the gamma form has a face-centered tetragonal lattice with 4 atoms in the unit cell. The structure of the delta form is unknown to the authors. The crystal parameter values (10) are: alpha 8.894 Å; beta 6.300 Å; gamma 3.774 Å, 3.526 Å. The alpha and beta forms are brittle and hard enough to scratch glass, but gamma manganese is flexible and soft, can be bent and cut with scissors, and cannot be ground in a mortar. Electrolytic gamma manganese changes to the alpha form at ordinary temperatures (11). The transformation requires 10 to 15 minutes to complete at 125°C. and about 20 days at room temperature, while at −10°C. no appreciable change occurs in 9 months.

Electrolytic manganese has been deposited in both the ductile and the brittle forms, sometimes under what appear to be the same conditions. Westgren and Phragmen (2), without describing their deposition process, stated that freshly deposited manganese has a simple X-ray pattern, is ductile, and becomes brittle in 14 days. Allmand and Campbell (12), in studying the electrodeposition of manganese under various conditions from both sulfate and chloride solutions, obtained only brittle deposits. On the other hand, Bradley (1), using the "optimum conditions" of Allmand and Campbell, obtained a little soft manganese with a face-centered tetragonal lattice in his first experiment. These conditions included the use of a cell with a rotating aluminum cathode and with two platinum anodes in porous pots, a catholyte of manganous and ammonium sulfates and an anolyte of ammonium sulfate, a current density of 110 amp./ft.^{2} (12.2 amp./dm^2) at a voltage of 7, and a catholyte temperature of 25°C. Brunke (13), however, obtained only brittle deposits with a similar method. Later, Brunke, using an electrolyte consisting of manganous and ammonium chlorides and 0.1 N hydrochloric acid, a current density of 185 amp./ft.^{2} (20.5 amp./dm.^{2}), and an aluminum cathode, obtained ductile deposits at first and less ductile ones as electrolysis proceeded. Herrmann (14), continuing the work of Brunke, prepared a ductile deposit of manganese which he identified as the gamma form. He also found that later deposits made from the same bath were less ductile. Subsequently, Herrmann modified the conditions by using an ammonium chloride solution as anolyte and prepared three or four deposits of gamma manganese. Bradt and

Oaks (15) and Fink and Kolodney (16) obtained hard manganese deposits on copper cathodes using various electrolytes such as (a) manganous and ammonium chlorides, (b) manganous and ammonium sulfates and ammonium thiocyanate, and (c) manganous and ammonium sulfates and glycerol.

The process used in the Bureau of Mines pilot plant for the production of electrolytic manganese (17) ordinarily results in hard, brittle alpha deposits. This process is carried out in a cell with stainless steel cathodes and with lead-silver anodes enclosed in canvas diaphragms. The electrolyte is composed of manganese sulfate and ammonium sulfate, contains 0.1 g. sulfur dioxide per liter, and is purified in two steps. The heavy metals are first removed by precipitation as sulfides with hydrogen sulfide at a pH of 6.0 to 6.5, and then the residual sulfides and colloidal materials are taken out of the resulting solution with ferric hydroxide formed by adding a small amount of ferrous sulfate and aerating the solution. It was observed (18) that in several instances the manganese deposits were ductile. This phenomenon was connected with the absence of sulfur dioxide; and in later experiments, gamma manganese with porous surface was deposited at low current efficiency from electrolyte prepared and purified in the usual way but containing no sulfur dioxide. Koster (19) reported that gamma manganese can be deposited from solutions without addition reagents and that the deposits redissolved after about 4 hours of plating time.

These observations and the need for samples suitable for use in studying physical properties led to the development of the method by which gamma manganese can be deposited consistently in good physical condition at good current efficiencies.

ELECTRODEPOSITION OF GAMMA MANGANESE

The method developed for producing gamma manganese differs from the regular Bureau of Mines process for the electrodeposition of manganese in that neither sulfur dioxide nor hydrogen sulfide is used in the preparation of the electrolyte and that copper is substituted for stainless steel as the cathode material.

The cells (Fig. 1) were constructed of wood lined with sheet lead and had the following inside dimensions: width, 9.5 in. (24.1 cm.); depth, 8 in. (20.3 cm.); height, 10.75 in. (27.3 cm.). Each cell contained two cathodes of 25-gauge electrolytic tough pitch copper (rolled and light-annealed) and three anodes made of 0.125-inch-thick lead-silver or lead-silver-arsenic alloy. The submerged cathode surfaces measured approximately $2\frac{3}{8}$ in. (6.0 cm.) by $5\frac{3}{16}$ in. (13.2 cm.), providing a cathode area of 0.34 ft.^{2} per cell. The cathode-to-cathode distance was approximately 3 in. (7.7 cm.). The submerged anodes had approximately the same dimensions but were bored with enough evenly spaced $\frac{3}{8}$-in. (.95 cm.) holes to reduce the anode surface per cell to one-half the cathode surface. The anodes were enclosed in 8-oz., single-filled canvas diaphragms, and each anode compartment had an overflow tube $9\frac{1}{2}$ in. (24.1 cm.) from the cell bottom through which the spent electrolyte flowed from the cell. The anolyte and catholyte volumes per cell were 2 and 9 liters, respectively. The agitators consisted of glass shafts extending to the bottoms of the cells with $1\frac{1}{4}$-in. (3.2 cm.) rubber

vanes spaced 1 in. (2.5 cm.) apart. At each side of the cell were glass or lead tubes through which water could be pumped to regulate the cell temperature. Power was furnished by a motor-generator set, and one or two cells were connected in series with an ammeter and a copper coulometer. A glass electrode pH meter was used in determining hydrogen-ion concentration.

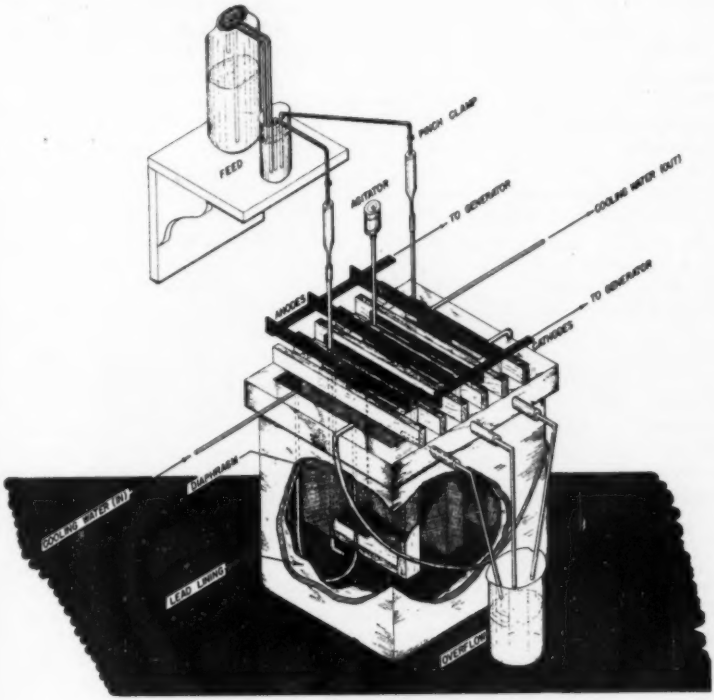

FIG. 1. Electrolytic manganese cell

The feed solutions, containing approximately 35 g. of manganese as manganese sulfate and 125 g. of ammonium sulfate per liter, were prepared with electrolytic manganese, C. P. sulfuric acid, commercial grade ammonium sulfate, and distilled water; C. P. ammonium hydroxide was used in adjusting the pH. The only purification consisted of aeration for 2 hours at a pH of 7.5, followed by filtration. At the beginning of each series of runs, the initial cell solution was prepared by diluting a portion of feed with distilled water and ammonium sulfate so that the manganese concentration was lowered to 20 or 25 g./l. while the ammonium sulfate concentration remained unchanged.

The cells were operated at a current density of approximately 35 amp./

ft.^{2} (4 amp./dm.^{2}) about 3.9 v., and a catholyte temperature of 30°C. for deposition periods of 5 to 12 hours. The feed pH was 7.0 to 7.4 and the catholyte pH was 7.4 to 7.7. Feed solution, entering the cell at the rate of approximately 350 ml./hr., was stripped of about one-half its manganese content before it flowed through the diaphragms into the anode compartments and then out of the cell through the overflow tubes. Shortly before they were placed in the cells, the cathodes were washed with carbon tetrachloride and polished with No. 1 metallographic paper. Edge effects were prevented by the use of edge sticks or by painting the edges of the cathodes with a solution of cellulose acetate in acetone or with glyptal insulating paint. Small sections of the cathodes above and below the solution lines also were painted to prevent corrosion. At the end of each run the cathodes were removed from the cell, quickly washed with water, dipped in a dilute solution of potassium dichromate for a second or two, and again washed with water. Finally they were dried, weighed, and stripped. Between runs the electrolyte was drained from the cells, filtered, and stored in glass bottles.

In a group of seven runs with two cells in series, 942.1 g. of manganese were deposited in 55.30 hr. at an average current efficiency of 68.3 per cent. The deposition time for each of the seven runs ranged from 7.00 to 10.25 hr., and the current efficiency varied from 71.6 per cent for the short runs to 61.7 per cent for the longer ones. In another series of 16 runs with one cell, 1004.2 g. of manganese were deposited in 143.38 hr. at an average current efficiency of 62.4 per cent; the deposition time ranged from 5.70 to 12.18 hr., and the current efficiency again dropped as the deposition time increased. This decrease in current efficiency with deposition time was caused, at least in part, by the tendency of the sheets of manganese to become loose from the cathodes and redissolve slightly. The deposits were bright, smooth, flexible, and nonporous with only occasional pin holes, and could be stripped easily in sheets by flexing the cathodes (Fig. 2A). The backs of some of the manganese sheets had a faint copper color.

The allotropic form of the deposits was determined by means of X-ray diffraction patterns made with Debye-Scherrer-Hull, 7.14-cm.-radius, full circular cameras. Iron radiation was used without filters, and the specimens were either wire-shaped solids or powders. The patterns for these deposits showed a face-centered tetragonal lattice; Fig. 4A shows a typical pattern with strong lines corresponding to interplanar spacings of 2.13, 1.89, 1.29, and 1.13 Å. The following lattice constants were calculated for another sample: parameter a = 3.774 Å, axial ratio 0.938. No evidence of the presence of alpha manganese was found in the patterns. The lines in these diffraction patterns were rather broad, probably as a result of variation in the parameters caused by hydrogen (20) in the metal. The sheets of manganese could be kept flexible and in the gamma form almost indefinitely by storing them in the freezing compartment of a refrigerator.

CODEPOSITION OF IMPURITIES

Gamma manganese prepared under the conditions described above contains more lead and copper and less sulfide sulfur than alpha manganese, as shown by the first three analyses in Table I. When the copper color

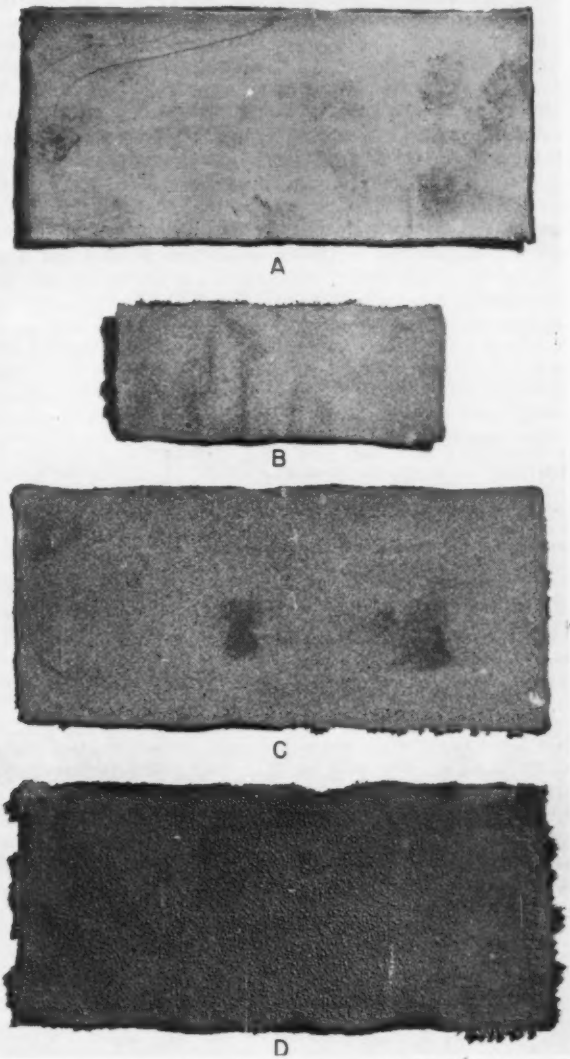

FIG. 2. Gamma manganese deposits. A. Prepared in lead-lined cells, lead-silver anodes. B. Prepared in glass cell, platinum anodes. C. Prepared in paraffin-lined cell, lead-silver anodes, 11 hour deposit. D. Prepared in paraffin-lined cell, lead-silver anodes, 24 hour deposit.

on the back of a gamma deposit (Group C) was polished off, the total copper content of the metal was lowered by only 0.005 per cent indicating that the remainder of the copper had been codeposited.

The codeposited lead was presumed to come from the lead lining of the cell, since lead sulfate is known to be slightly soluble (21) in concentrated ammonium sulfate solutions, and experience with manganese electrolytes proves that they pick up lead. The deposition of lead-free gamma manganese was investigated, therefore, with electrolyte prepared as described above but kept from contact with lead. In the first tests, carried out in a one-liter glass cell containing a copper cathode and two platinum anodes, 60.2 g. of flexible, low-lead manganese were made (Group D, Table I). These deposits did not look like the gamma deposits made before but had the crystalline appearance of alpha manganese (Fig. 2B). However, X-

TABLE I. *Impurities in typical manganese deposits*

Group	Form of deposit, conditions	Impurity codeposited, per cent			
		Pb	Cu	Total sulfur	Sulfide sulfur
A	Alpha; prepared in small lead-lined cells, 0.5 g. SO_2 per liter added to feed.	0.005	0.002	0.089	0.086
B	Alpha; prepared in Boulder pilot plant, 0.1 g. SO_2 per liter added to feed.	—	—	0.046	0.041
C	Gamma; prepared in lead-lined cell, lead-silver anodes.	0.3*	0.02	0.01	0.008
D	Gamma; prepared in glass cell, platinum anodes.	0.02	**	0.007	0.006
E	Gamma; prepared in paraffin-lined cell, lead-silver anodes; short deposit	0.02	0.01	0.005	0.003
F	Gamma; prepared in paraffin-lined cell, lead-silver anodes; long deposit	0.02	0.004	0.008	0.006

* The lead content was sometimes twice as great at the beginning of a series of runs before the impurity concentrations in the electrolyte came to equilibrium.

** These deposits had 0.1 per cent Cu, chiefly on the back of the sheet.

ray examination (Fig. 4B) showed that they contained only the gamma form. Although the sheets of manganese could be stripped from the cathodes, they were very tightly attached to them and appreciable amounts of copper remained on the backs of the manganese sheets. The relatively high copper content of these deposits is believed to represent metal on the backs of the deposits rather than codeposited metal. These were the only experiments in which gamma deposits adhered so tightly to the cathodes; this may have been caused by the large quantities of manganese oxides formed as a result of the use of platinum anodes.

One of the large cells (Fig. 1) was lined with paraffin, equipped with lead-silver anodes, and used in a second series of tests. First, a total of 246 g. of flexible, low-lead manganese (Group E, Table I) were deposited at a current density of 30 amp./ft.^{2} (3.3 amp./dm.^{2}) and a current efficiency of 55 per cent in four tests varying in length from 6 to 12 hours. These deposits had a crystalline appearance (Fig. 2C), and the backs of the sheets frequently had a copper tint. When this copper color was polished off,

the total copper content of the metal was lowered by 0.005 to 0.01 per cent, depending on the intensity of the original color. Second, 550 g. of flexible, low-lead manganese were made in five long-time deposits (19.6 to 26.5 hr.) at an average current efficiency of 41.2 per cent (Group F, Table I). In several of these tests, the pH of the catholyte was raised to 7.9, and 0.5 g./l. of hydroxylamine sulfate was added to the feed to inhibit the oxidation of manganese. The surfaces of these deposits were rougher than those of the shorter-time tests (Fig. 2D). Since all of the manganese produced in these tests was flexible, it was presumed to be in the gamma form.

To investigate the codeposition of copper with gamma manganese, a series of 6- or 7-hour tests was carried out in a one-liter glass cell with lead-silver-arsenic anodes and a copper cathode, using gamma electrolyte to which various amounts of copper were added as copper sulfate. With feed solution containing copper in concentrations up to 30 mg./l. the deposits were bright, smooth, and flexible and had the crystalline appearance of low-lead gamma manganese. The sheets of manganese stripped well, and the backs frequently had the copper color. This color was no stronger, however, than was present when no copper was added to the electrolyte, and experiment proved that it was equivalent to only 0.005 per cent copper. When the feed solution contained 15 mg. of copper per liter, the deposits contained 0.11 per cent copper, and when it contained 30 mg., 0.17 per cent copper was codeposited. The current efficiencies dropped from 62.3 per cent with no copper added to the feed solution to 43.4 per cent with 30 mg./l. When the copper concentration was 60 mg. or more, little or no metallic manganese was deposited.

CATHODES AND CATHODE PREPARATION

The nature of the cathodes and their preparation were found to be important in the electrodeposition of gamma manganese. Deposits made on brass cathodes and on cathodes of stainless steel or iron electroplated with copper gave results similar to those obtained with copper cathodes, with a slight improvement in current efficiency. But when 18-8 stainless steel cathodes, which are commonly used in the deposition of alpha manganese, were used the results were unsatisfactory. Although the manganese deposits were soft and flexible, they were usually porous (Fig. 3) and tended to become loose from the cathode so that partial or complete resolution often resulted. Deposits made on copper cathodes with extra-smooth surfaces (polished with No. 4/0 metallographic paper) tended to become loose. The use of stainless steel cathodes finished with No. 3/0 paper resulted in deposits that were either very porous sheets or consisted of a series of discontiguous crystals which could be rubbed off with the fingers.

EFFECT OF SULFIDES, SULFUR DIOXIDE, AND DITHIONATE ON THE DEPOSITION OF GAMMA MANGANESE

There was no conclusive evidence that both the sulfide purification and the use of sulfur dioxide as an addition reagent must be eliminated to deposit gamma manganese. It was of particular interest to know if the omission of the sulfide purification is essential because this purification is important when electrolyte is prepared from manganese ore. The individual

TABLE II. *Effect of sulfides and sulfur dioxide*

Group of runs	Special treatment of electrolyte	Total deposition time (hours)	Number of runs in group	General description of deposits	Typical runs							
					Group deposition time before the run (hours)	Deposition time (hours)	Current efficiency (per cent)	Description of individual deposits	Impurities codeposited (per cent)				X-ray analysis
									Pb	Cu	Total S	Sulfide S	
1	None	27.33	5	Flexible; stripped well but hard to start; copper color on backs of sheets.	7.58	6.75	66.5	Flexible; typical gamma.	0.095	0.035	0.005	0.005	—
					20.83	6.50	59.6	Do.	0.448	0.025	0.005	0.005	—
2	Cell and feed solutions treated with yellow $(NH_4)_2S$* and $FeSO_4$.	63.23	7	First 3 deposits (18.85 hours) brittle, next 2 deposits (24.63 hours) slightly flexible, last 2 deposits flexible. First 2 deposits did not strip, next 2 difficult to strip, last 3 stripped well.	0.0	6.50	58.8	Could not strip.	—	—	—	—	Alpha
					12.75	11.10	45.4	Brittle; difficult to strip; spongy.	<.005	—	0.011	0.009	—
					23.85	11.83	58.3	Slightly flexible; difficult to strip.	<.005	—	0.014	0.012	—
					48.48	4.17	67.1	Flexible; stripped well; became brittle quickly.	0.342	0.0091	0.014	0.014	—
					52.65	10.58	56.6	Do.	0.445	0.0079	0.019	0.019	—
3	Cell and feed solutions treated with yellow $(NH_4)_2S$*.	46.54	5	Slightly flexible; stripped well in one piece.	0	11.05	51.7	Slightly flexible; stripped well.	0.052	0.010	0.015	0.012	Gamma
					37.24	9.30	64.6	Do.	0.010	0.0070	0.016	0.014	Gamma (Fig. 4D)
4	Cell and feed solutions treated with colorless $(NH_4)_2S$**.	35.84	5	Longer deposits poor with much re-solution; all deposits flexible.	26.57	4.20	59.8	Flexible; some re-solution; stripped well.	<.005	0.011	0.011	0.011	—
					30.77	5.07	58.4	Flexible; became brittle quickly; stripped well.	<.005	0.0083	0.008	0.008	Gamma (Fig. 4E)
5	No treatment for cell solution; 0.5 gram SO_2 per liter of feed.	7.79	4	First deposit (3.73 hours) slightly flexible, others brittle. All except first deposit difficult to strip, sometimes only outer layer stripped.	9.91	10.03	56.9	Brittle; difficult to strip.	<.005	—	0.014	0.013	—
					19.94	17.85	53.4	Do.	<.005	—	0.021	0.017	Alpha (Fig. 4F)

* Amount $(NH_4)_2S$ equivalent to 0.4 grams H_2S per liter electrolyte.
** Amount $(NH_4)_2S$ equivalent to 0.5 grams H_2S per liter electrolyte.

effects of ammonium sulfide and sulfur dioxide were studied; since previous work (22) has indicated that a manganese electrolyte circuit to which sulfur dioxide is added will contain dithionate, the effect of dithionate was also studied.

The effects of using ammonium sulfide and sulfur dioxide were investigated with regular gamma electrolyte to which 0.5 g. hydroxylamine sulfate had been added. In the first group of tests, this electrolyte was used without special treatment. For the second group, the cell solution and a portion of feed at a pH of 6.85 were treated with yellow ammonium sulfide and activated charcoal followed by a 5-hour aging period and filtration. This was followed by the iron treatment which involves the addition of ferrous sulfate to the solution at a pH of 7.6, aeration for 3.3 hr., and filtration. Then the cell solution and a fresh portion of feed were given the sulfide treatment, but not the iron treatment, before use in the third group of tests. After the third group, the cell solution was given the iron purification and operated with regular electrolyte for 30 hours, making good gamma manganese during at least the last 23 hours. Then the cell solution and a portion of feed were treated with colorless ammonium sulfide but not with iron, and the fourth group of tests was carried out. For the last group of tests, the cell solution was given no treatment, and 0.5 g. sulfur dioxide was added to each liter of feed. The results of the various tests are summarized in Table II.

TABLE III. *Effect of dithionate and sulfur dioxide*

Test No.	Cell No.	Addition to feed and initial cell solution (grams per liter)	Current efficiency (per cent)	Impurities codeposited (per cent)			Description of deposit
				Pb	Sulfur		
					Total	Sulfide	
1	5	None	72.4	0.34	0.009	0.005	Flexible; stripped well.
	6		73.8	0.26	0.009	0.008	
2	5	0.4 SO_2	65.4	0.05	0.04	0.03	Crystalline appearance; brittle.
	6	0.5 S_2O_6	69.6	0.32	—	—	Flexible.
3	5	1.6 SO_2	58.7	0.01	0.2	0.2	Brittle; difficult to strip.
	6	2.0 S_2O_6	69.5	0.24	0.02	0.02	Flexible.
4	6	5.0 S_2O_6	66.9	0.2	0.013	0.012	Flexible.

Another series of tests was carried out with two cells in series to study the effects of dithionate and sulfur dioxide (Table III). Dithionic acid was prepared just before the beginning of each experiment and added to the electrolyte before there was any appreciable decomposition; dithionate is known to be stable (23) under the conditions of these experiments. All the tests were 7 hours long, and in each the initial cell solution was that drained from the cells at the end of the previous test.

All the manganese deposits were good, bright, and smooth with the exceptions noted in group 4, Table II. Flexible deposits, shown by X-ray examination to contain only the gamma form (Fig. 4E), were obtained when

the electrolyte was treated with colorless ammonium sulfide. Slightly flexible deposits were made with electrolyte treated with yellow ammonium sulfide. X-ray examination proved that these deposits were chiefly gamma with some alpha; in the pattern shown in Fig. 4D the strongest alpha line, corresponding to interplanar spacing 2.09 Å, was barely visible on the film. These deposits stripped in sheets, and were easily distinguishable

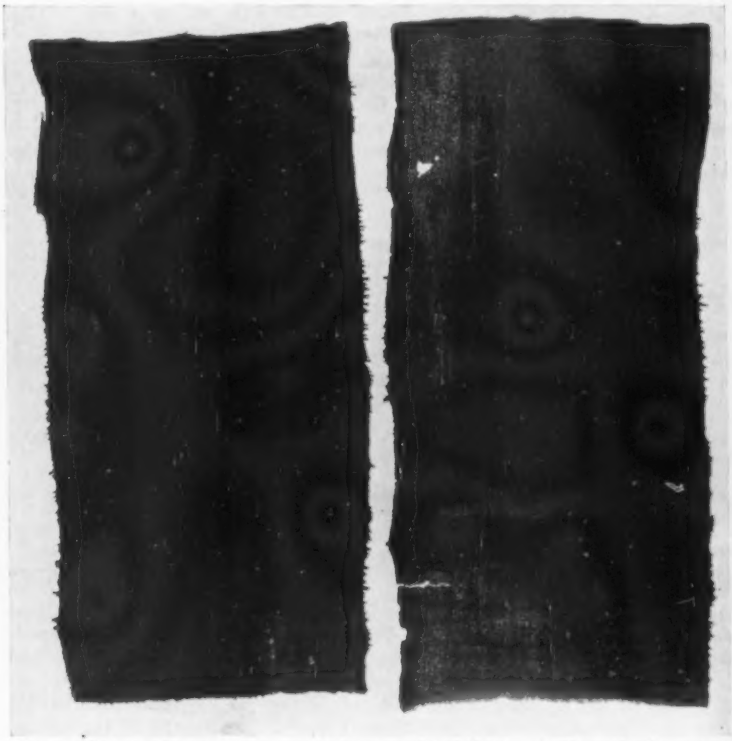

FIG. 3. Sheets of gamma manganese; transmitted light. A. Deposited on copper cathode. B. Deposited on stainless steel cathode.

from brittle deposits. Flexible deposits were prepared with electrolyte treated with yellow ammonium sulfide and iron, after a "breaking in" period during which first brittle (alpha, by X-ray examination) and then slightly flexible deposits were made. It should be noted that without the iron treatment (group 3, Table II) the deposits never varied from the slightly flexible condition. The iron treatment probably removed most of the colloidal sulfur formed during the yellow ammonium sulfide treatment, and the "breaking in" period further decreased the colloidal sulfur content of the cell solution until it was below some critical level. Flexible deposits

were also obtained with electrolyte containing dithionate. Brittle deposits, shown by X-ray analyses to contain only alpha manganese, were obtained with electrolyte containing sulfur dioxide. The pattern in Fig. 4F had lines corresponding to spacings 2.09, 1.21, 1.89 Å, and the parameter was

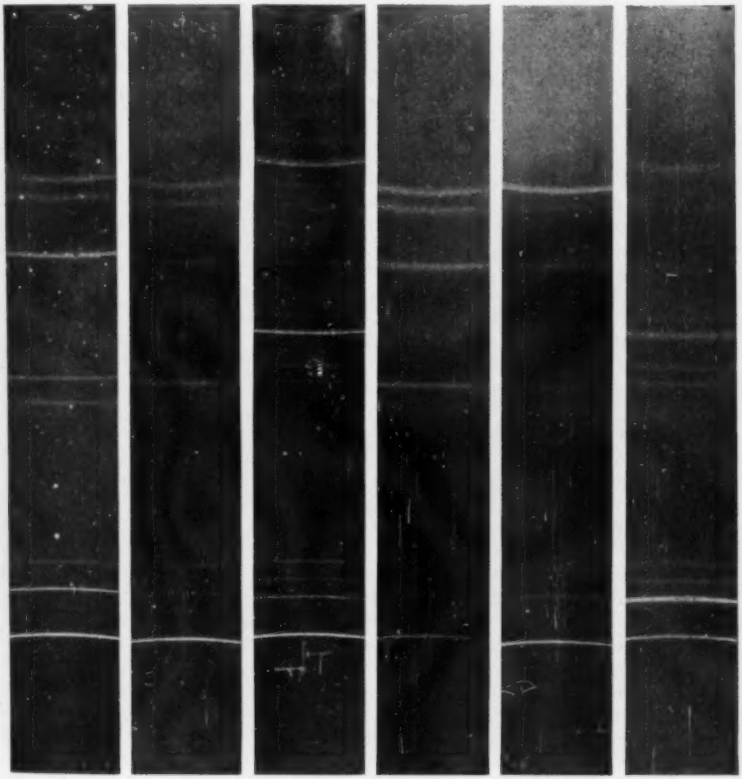

FIG. 4. X-ray diffraction patterns of manganese metal. In D the alpha line (2.09) referred to in the text is a faint line just above the strongest gamma line (2.13 A).

approximately 8.90 Å; a standard alpha pattern is included for comparison (Fig. 4C). Throughout this work, X-ray examination always proved that flexible deposits were in the gamma form and brittle ones in the alpha form. For this reason it was considered valid to classify some of the deposits in Table II and all in Table III as gamma or alpha solely on the basis of flexibility.

Sulfide purification resulted in deposits relatively high in sulfide sulfur, and sulfide purification without the iron treatment resulted in deposits low in lead. Alpha deposits on copper cathodes were difficult to strip.

It may be concluded, therefore, that the addition of sulfur dioxide to the electrolyte prevents the formation of gamma manganese but the addition of dithionate does not. Furthermore, the use of sulfide purification does not prevent the deposition of gamma if the concentration of colloidal sulfur is kept low enough.

DEPOSITION OF ALPHA MANGANESE ON GAMMA MANGANESE STARTING SHEETS

Gamma manganese prepared under favorable conditions retains its flexibility for several days at ordinary room temperatures, remains flexible almost indefinitely if stored in a refrigerator, and can be cut with shears, punched, or drilled. The use of starting sheets of gamma manganese in the deposition of ordinary alpha manganese would be an interesting and possibly valuable way to utilize these properties. This possibility was investigated with sheets of gamma manganese which were prepared as described under "Electrodeposition of Gamma Manganese" in runs 7 or 8 hours long and which were stored in the freezing compartment of a refrigerator before being used. Just before they were placed in the cell, the sheets were washed with carbon tetrachloride and polished with No. 1 metallographic paper. Stainless steel clips were used to support the cathodes in the cell, and cellulose acetate dissolved in acetone was used to prevent corrosion in the areas around the solution line and above the solution line within reach of cell spray. The deposition of alpha manganese was carried out in an ordinary manganese cell containing three lead-silver anodes in canvas diaphragms and two gamma manganese starting sheets with a total effective area of 0.22 ft.^{2} (204 cm.^{2}). The electrolyte had the usual composition, was purified by aerating for 2 hours at a pH of 7.5 and then precipitating the heavy metals with ammonium sulfide at a pH of 6.8, and contained 0.5 g. sulfur dioxide per liter. During a 24-hour run made at a current density of 23 amp./ft.^{2} (2.5 amp./dm.^{2}) and a catholyte temperature of 30°C., 80.9 g. of alpha manganese were deposited at a current efficiency of 63.6 per cent. The deposit was bright, smooth, and normal in appearance except for the trees at the edges resulting from the fact that no edge strips were used (Fig. 5). At the end of the experiment the starting sheets were still flexible enough to be handled without special care.

A few tests were also made to study methods for suspending and connecting starting sheets of gamma manganese in a cell. The sheets used in these tests were 5¼ in. (13.3 cm.) long, 2½ in. (6.4 cm.) wide, and 0.010 to 0.016 in. (.03 to .04 cm.) thick. They contained 0.005 per cent sulfur, 0.01 to 0.02 per cent copper, and 0.02 or 0.3 per cent Pb. Before being used in the tests, the sheets had been stored for 6 weeks or more in the freezing compartment of a refrigerator. One of the sheets was bolted to a stainless steel clip (Fig. 6A), and another was riveted to an aluminum bus bar with cold, hollow aluminum rivets (Fig. 6B). Both of these sheets were still flexible after 3 days at room temperature but were noticeably less flexible after 6 days. The third sheet was bent into a loop and the loop secured with hollow aluminum rivets (Fig. 6C). After 3 days at

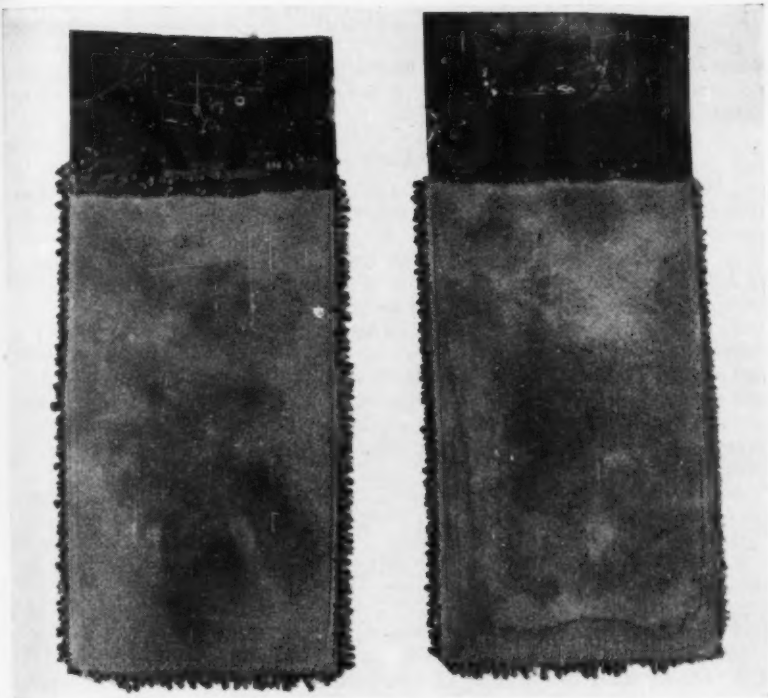

FIG. 5. Deposits of alpha manganese on gamma manganese starting sheets

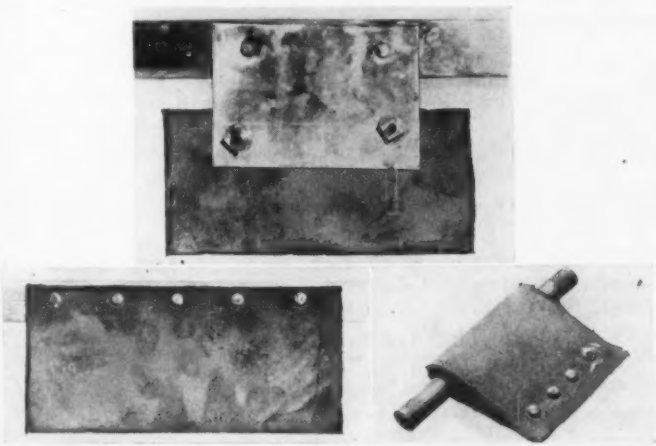

FIG. 6. Suspending and connecting gamma manganese starting sheets. A. In stainless steel clip. B. Riveted to aluminum bus bar. C. Riveted in loop.

room temperature the manganese was still somewhat flexible but much less so than the first two sheets, and between the third and sixth days the sheet broke at the bend.

CONCLUSIONS

1. Gamma manganese can be electrodeposited from aqueous solutions of manganese and ammonium sulfates at current efficiencies of 62 to 72 per cent.
2. Gamma manganese deposits on copper or brass are bright, smooth, and flexible and strip readily in non-porous sheets. Stainless steel is much less satisfactory than copper or brass as a cathode material.
3. The gamma manganese deposits normally contain 0.005 to 0.008 per cent sulfide sulfur and 0.01 to 0.02 per cent copper. The addition of 30 mg. copper per liter to the electrolyte results in deposits containing 0.17 per cent copper; with 60 mg. copper per liter, no metallic manganese was obtained. The gamma manganese contained 0.02 per cent lead when prepared in cells without lead linings and 0.3 per cent lead when prepared in lead-lined cells.
4. Gamma manganese can be deposited from electrolyte to which dithionic acid or hydroxylamine sulfate has been added and from electrolyte purified with colerless ammonium sulfide.
5. Purification with yellow ammonium sulfide alone results in deposits that are only slightly flexible and contain some alpha manganese. Purification with yellow ammonium sulfide following by a treatment involving precipitation of iron hydroxide, however, results in flexible gamma deposits without detectable amounts of alpha.
6. The presence of sulfur dioxide in the electrolyte causes the manganese to deposit only in the brittle alpha form.
7. Sheets of gamma manganese can be cut, drilled, punched, riveted, bolted, and bent and can be used as starting sheets for the deposition of alpha manganese.

ACKNOWLEDGEMENTS

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Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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THE ELECTRODEPOSITION AND PROPERTIES OF TIN-ZINC ALLOYS[1]

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ABSTRACT

Tin and zinc can be co-deposited in all proportions from solutions containing sodium stannate, sodium hydroxide, sodium zinc cyanide, and free sodium cyanide, operated at 65°C. and at a cathode current density, for still solutions, of 10–30 amp./ft.^{2} (1.08–3.24 amp./dm.^{2}) using alloy anodes of the same composition as the alloy to be deposited. The tin content of the solution is maintained at 30 g./l. and the free cyanide at 17.5–20.0 g./l. throughout, and the composition of the deposit is adjusted by varying the amounts of zinc, total cyanide, and sodium hydroxide. The most serviceable composition from the viewpoint of the protection afforded to steel is around 78 per cent tin-22 per cent zinc. Plate of this composition, not less than 0.0003 in. thick, is superior in protective value to either cadmium or zinc plate of comparable thickness, and moreover is extremely easy to solder. With less than 78 per cent of tin the corrosion resistance of the plate diminishes but is not seriously impaired until the tin content falls below 50 per cent. The electrodeposition of alloys containing less than 50 per cent of tin presents greatly increased operating difficulties and it probably is more economical to apply those alloys by hot dipping. Tin-zinc plate can be passivated by immersion in hot 2 per cent chromic acid solution. Passivation further increases resistance to corrosion and reduces any tendency toward finger-marking. The properties and uses of tin-zinc plate are briefly discussed. The 78 per cent tin alloy is being increasingly used as an alternative to cadmium.

INTRODUCTION

A summarized account of the pioneer work carried out at the Tin Research Institute on the electrodeposition of tin-zinc alloys was published some two years ago by R. M. Angles (1). Since that time further work on

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this subject has been undertaken in the laboratory, and tin-zinc plating has advanced to a stage where it is being developed on an industrial scale. Much has been learned since the first paper was published, and some of the conclusions then reached have called for modification in the light of more recent experience. Some of the results obtained in the early exploratory work have not hitherto been published, and, in view of the widely increasing interest which this process is now attracting, it has been decided to place on record both this information and such other relevant details of theory and practice as are necessary for the proper understanding of the process.

The metals tin and zinc are widely used as coatings for the protection of steel against corrosion. Under ordinary atmospheric conditions steel is anodic to tin and cathodic to zinc. Tin itself is resistant to atmospheric corrosion and a continuous tin coating on steel should therefore afford permanent protection against rusting. Zinc protects by sacrificial action, being itself consumed in the process, but although even discontinuous zinc coatings will give protection at the outset, rusting becomes inevitable after a certain amount of the zinc has been consumed. Commercial hot-dipped and electrodeposited tin coatings are almost invariably porous to an extent depending partly on their thickness, and consequently with all but the thickest coatings rusting occurs sooner or later and spreads from the pore sites. Hitherto, no method of insuring complete freedom from porosity in thin tin coatings has been devised, and it is not surprising, therefore, to find that zinc, especially in view of its lower cost, is more favored for the protection of steel out-of-doors. That zinc is far from ideal for the purpose will be apparent from the foregoing remarks. A reduction in the porosity of tin coatings or in the rate of sacrificial attack of zinc coatings would insure more lasting protection of the steel. It may not be possible to realize these ideals fully in the case of the pure metal deposits but they might be approached by resorting to composite coatings containing both metals. Electrodeposited alloys are usually finer grained than their components deposited under comparable conditions, and it is therefore reasonable to expect that alloying tin with zinc will lead to some refinement of structure and hence possibly to some reduction in porosity. Comparison of Fig. 1 and 2 reveals the superior structure of tin zinc plate as compared with that of tin deposited under parallel conditions. Alloying also modifies the electrochemical properties of the coating and affords a means of adjusting its reactivity with respect to the steel or other basis metal.

The idea of co-depositing tin and zinc is not new and appears to have originated in 1915 when Marino (2) applied for a patent covering an electrodeposition process which embraced this alloy among several others. Since that date, a number of further patents bearing directly or indirectly on tin-zinc plating have appeared, but so far as can be ascertained no serious attempt to exploit tin-zinc plating outside the laboratory was made prior to the development of the process described in this paper. As none of the processes hitherto suggested was entirely satisfactory from the commercial viewpoint, this slow progress is understandable, and it was not until Lowinger, Angles, and Baier (3) patented the use of polarized tin-zinc alloy anodes in conjunction with a sodium stannate-sodium zinc cyanide type of bath that any real advance was made. Following this a thorough in-

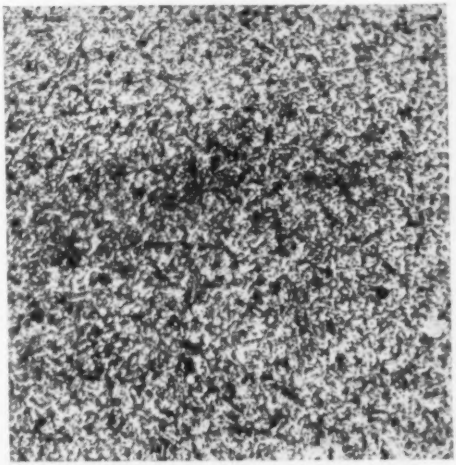

FIG. 1. Microstructure of electrodeposited tin-zinc plate (80 per cent tin). Etched in 5 per cent trichloracetic acid. 650×.

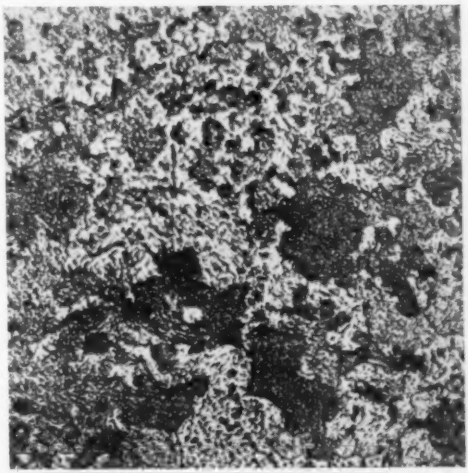

FIG. 2. Microstructure of tin deposited from the sodium stannate bath. Etched in 5 per cent trichloracetic acid. 650×.

vestigation of the deposition and properties of tin-zinc plate was made and as a result a practical process for depositing the more serviceable alloys was developed.

For applications where the maximum degree of protection is demanded

and where solderability, smoothness, and appearance are considerations, tin-zinc plate should contain 75–80 per cent of tin. This is the composition now being developed. Some attention has been given to the deposition of alloys containing 50 per cent of tin and details of a process have been worked out. Compared with the high-tin alloys the 50 per cent tin alloy is somewhat less protective and less easy to solder but has the advantage of being a cheaper coating. There are technical difficulties in depositing alloys of so high a zinc content and so far they have not been used on an industrial scale. Alloys containing less than 50 per cent of tin will not be considered in this paper.

THEORETICAL CONSIDERATIONS

Tin and zinc can be co-deposited from simple salt and from complex ion solutions. For depositing alloys containing 50 per cent or more of tin, however, only complex solutions have proved to be practicable. The normal electrode potentials of tin and zinc at 25°C. expressed on the hydrogen scale are −0.136 volt and −0.758 volt, respectively. These figures, of course, refer to the potentials attained in solutions of normal metal ion concentration and under static conditions, and are susceptible to considerable modification under conditions of electrolysis where the electrode processes are no longer thermodynamically reversible. Nevertheless, a difference of more than 0.6 v. between the static equilibrium potentials is sufficiently large to suggest that co-deposition of the two metals from acid solutions of their simple salts may be impracticable. Preliminary experiments made with mixed sulphate baths have proved that this is so; the tin tends to deposit much more readily than the zinc, and a very large amount of zinc has to be added to the electrolyte to cause any appreciable quantity of that metal to deposit with the tin. Fig. 3 shows that the addition of even as much as 50 g./l. of zinc to a standard stannous sulphate-cresolsulphonic acid bath has little effect on the form of the cathode potential-current density curve. In order to deposit alloys containing more than a few per cent zinc, the deposition of the tin must be retarded, and it becomes necessary to resort to complex solutions of low metal ion concentration in which the deposition potentials of the two metals are nearer to one another.

The solutions at present in use for tin-zinc plating are in reality a combination of the sodium stannate tin-plating bath and the zinc cyanide zinc-plating bath, and, in addition to the two metal salts, therefore, contain free sodium hydroxide and free sodium cyanide.

When depositing tin from a bath containing sodium stannate and free sodium hydroxide the following reactions occur:

$$Na_2SnO_3 \rightarrow 2Na^+ + SnO_3^{--} \quad (1)$$

$$SnO_3^{--} + 3H_2O \rightleftharpoons Sn^{++++} + 6OH^- \quad (2)$$

In cyanide zinc plating practice the basic reactions are:

$$2NaCN \cdot Zn(CN)_2 \rightarrow 2Na^+ + Zn(CN)_4^{--} \quad (3)$$

$$Zn(CN)_4^{--} \rightleftharpoons Zn^{++} + 4CN^- \quad (4)$$

$$Na_2ZnO_2 \rightarrow 2Na^+ + ZnO_2^{--} \quad (5)$$

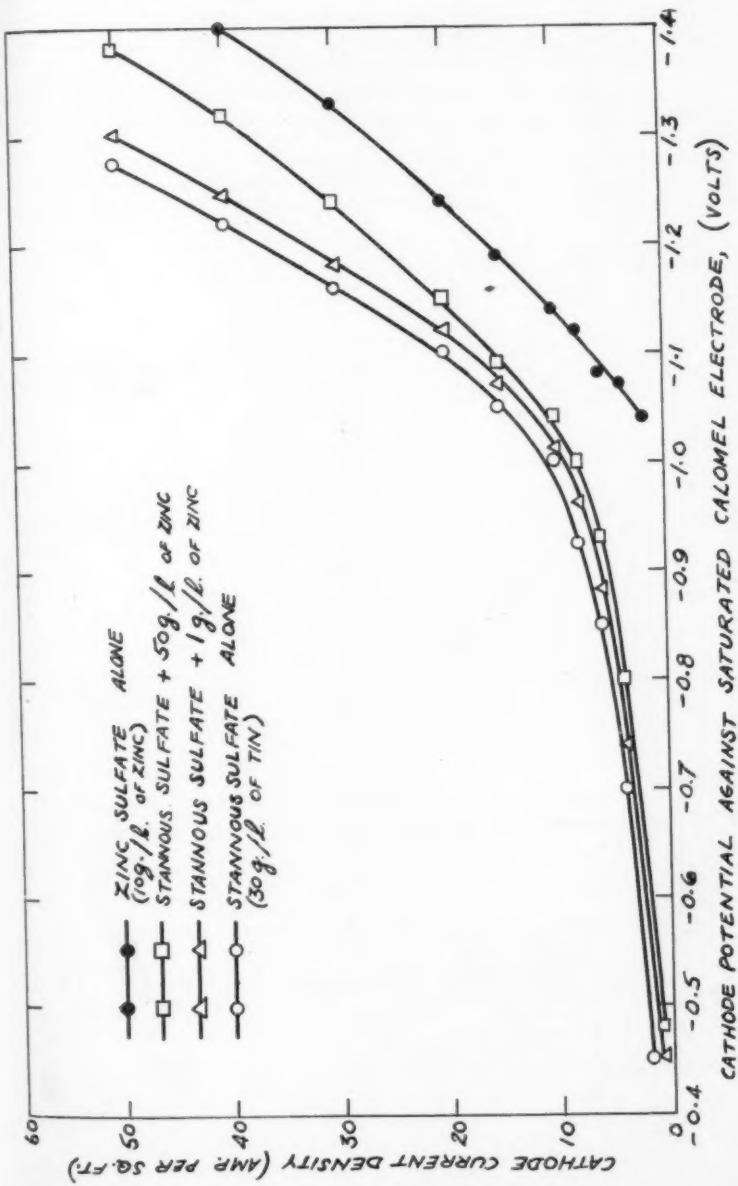
ZINC SULFATE ALONE (10g./l. of ZINC)
STANNOUS SULFATE + 50g./l. of ZINC
STANNOUS SULFATE + 1g./l. of ZINC
STANNOUS SULFATE ALONE (30g./l. of TIN)
CATHODE CURRENT DENSITY (AMP. PER SQ. FT.)
CATHODE POTENTIAL AGAINST SATURATED CALOMEL ELECTRODE, (VOLTS)
60
50
40
30
20
10
0
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
-1.3
-1.4

FIG. 3

$$2H_2O + ZnO_2^{--} \rightleftharpoons Zn^{++} + 4OH^- \quad (6)$$

$$Zn(CN)_4^{--} + 4OH^- \rightleftharpoons ZnO_2^{--} + 4CN^- + 2H_2O \quad (7)$$

In tin-zinc plating from a mixed electrolyte the possibility of all of these reactions taking place must be considered. From reaction (2) an increase

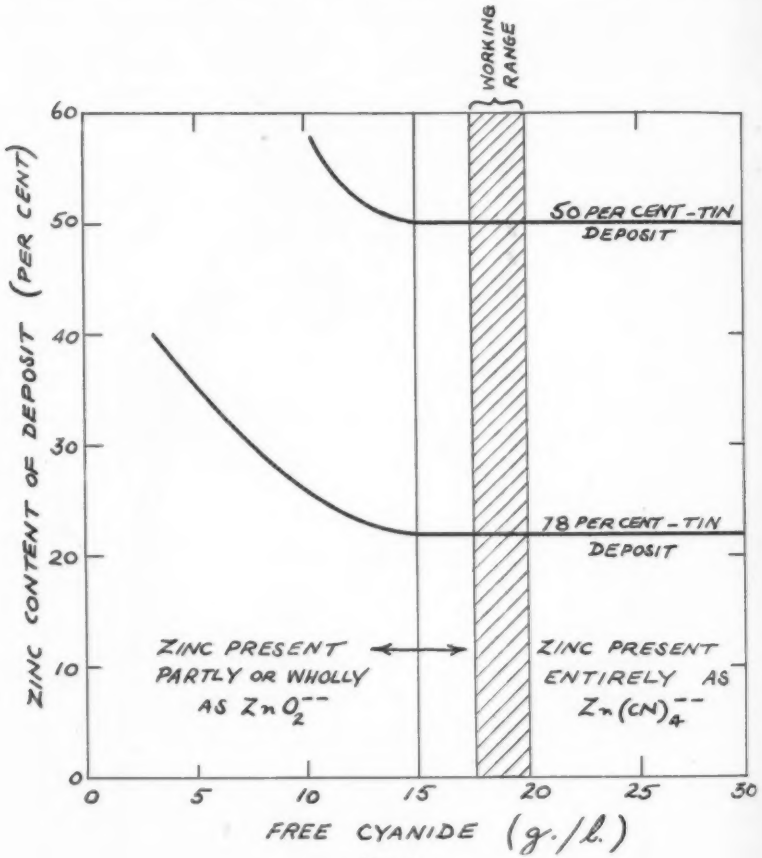

FIG. 4

in the sodium hydroxide content of the electrolyte would be expected to lead to a decrease in the tin content of the deposit and this is borne out in practice, the relationship being approximately linear (Fig. 5). If, on the other hand, the free sodium cyanide content of the electrolyte is increased, the amount of zinc in the plate at first diminishes rapidly, but after a certain fairly critical concentration has been reached further increase in cya-

nide has little influence on the composition of the deposit (Fig. 4). Further reference to this effect will be made later; meanwhile, it may be stated that the form of the composition-cyanide concentration curve is attributed to the presence of the two zinc-containing anions.

The efficiency of deposition is much higher for a straight zincate bath than for a straight zinc cyanide bath. Partly as a result of this observation, the view has been expressed that in a zinc plating solution containing zinc cyanide, free cyanide, and free hydroxide, the ZnO_2^{--} anion predominates, and that this anion is in fact a more favorable source of zinc ions than the

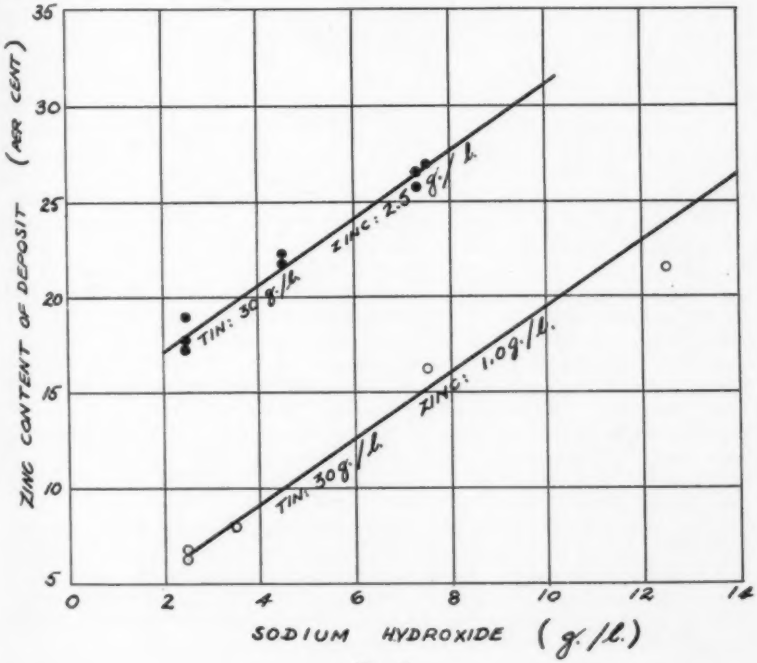

FIG. 5

alternative anion $Zn(CN)_4^{--}$ (4). It does not follow, however, that ZnO_2^{--} plays an equally important part in the deposition of tin-zinc alloys from solutions of the type under consideration. It is certainly possible to co-deposit tin and zinc from solutions containing only sodium stannate, sodium zincate, and free sodium hydroxide, but in the absence of the cyanide the deposits are invariably high in zinc. To enable alloys of higher tin content and controlled composition to be deposited, the presence of free sodium cyanide in the bath is essential and the amount of free cyanide must equal or exceed the critical concentration already mentioned.

From the available evidence it seems that the ZnO_2^{--} anion is much less

stable than the $Zn(CN)_4^{--}$anion.[2] An increase in free cyanide concentration is accompanied by a decrease in zincate ion concentration, as shown in equation (7), and ultimately the $Zn(CN)_4^{--}$anion only takes an active part in the electrolysis. The form of the free cyanide-deposit composition curve supports this contention. The initial, steeply-falling part of the curve corresponds to deposition of the zinc wholly or in part from zincate ions, and the point of inflexion occurs when sufficient cyanide has been added to reduce the zincate ion concentration practically to zero. Thereafter, the deposition of the zinc takes place almost entirely through the medium of the $Zn(CN)_4^{--}$ion. Under these conditions it would be expected that the efficiency of deposition of the zinc would be lower than when zincate ions were present; but on the contrary, a wide variation in the concentration of the free cyanide is found to have little effect on the efficiency of alloy deposition. An increase in free cyanide reduces the zinc ion concentration and tends to lower the cathode efficiency and raise the cathodic polarization for the zinc. However, with large additions of cyanide, the accompanying increase in pH raises the reversible potential of hydrogen discharge with a resulting trend towards a higher efficiency which to some extent offsets the counter effect of the lower zinc ion concentration. This explanation may not fully account for the observed constancy of efficiency with variation in the free cyanide content of the bath. Other considerations are the mutual influence of the two depositing metals on one another and the possible lowering of the deposition potential of the zinc by the presence of the tin. A different interpretation must be put on cathode efficiency determinations when depositing an alloy on the one hand and one of its constituent metals on the other. In tin-zinc plating it must be borne in mind that only 20–50 per cent of the cathode deposit is zinc, and hence, for a given cathode current density, the rate of removal of zinc ions from the cathode layer is only 20–50 per cent of the rate when depositing pure zinc. The integrated result of all these possibilities is that there is no appreciable change either in the cathode efficiency or in the zinc content of the deposit over a range of approximately 15–30 g./l. of free cyanide. The cathode efficiency does not remain constant when the hydroxide concentration is varied, however, but diminishes as the amount of hydroxide is increased. There is now no directly compensating factor as in the case of the cyanide, and when depositing alloys high in zinc it thus becomes necessary, in addition to increasing the hydroxide, to increase the zinc content of the bath in order to restore the efficiency so far as possible.

It is thus apparent that a wide range of tin-zinc alloys can be deposited from solutions containing sodium stannate, sodium zinc cyanide, sodium

[2] For potassium zinc cyanide solutions the value of the dissociation constant, K, of the equilibrium $K = \frac{[Zn^{++}][(CN)^-]^4}{[Zn(CN)_4^{--}]}$ is given by Euler (*Ber.*, **36**, 3400, 1903) as 1.3×10^{-17} and by Britton and Dodd (*J. Chem. Soc.*, 1940, 1932) as $10^{-19} - 10^{-20}$, and it thus seems that $Zn(CN)_4^{--}$has a fairly high stability. No corresponding value for sodium zincate could be found, but it is noteworthy that Thorne and Ward ("Inorganic Chemistry", Gurney and Jackson, London, 1939) express the view that zincates and some allied compounds are probably not true compounds but sols formed by the peptization of the hydroxides. They observe that the heavy metal portions of these compounds will not diffuse through parchment paper and, therefore, conclude that these portions are entirely colloidal in character, and not ionic or in ordinary solution.

hydroxide, and free sodium cyanide merely by altering the proportions of these four constituents. It is convenient in practice to keep the tin and free sodium cyanide contents of the bath constant and adjust the composition of the deposit by varying the amounts of sodium zinc cyanide and sodium hydroxide. In this way tin and zinc can be co-deposited in any desired proportions.

INFLUENCE OF THE VARIABLES OF THE PROCESS ON THE CATHODE DEPOSIT

When this investigation was begun little was known of the properties of tin-zinc alloys, except that tin-zinc foil containing 92 per cent tin had been used with satisfactory results for milk bottle closures (5). It was therefore decided first to study the deposition of alloys of this, the eutectic, composi-

TABLE I. *Influence of the concentrations of tin and zinc in the solution on the composition of the cathode deposit and efficiency of deposition*

Temperature: 70°C. Current density: 10 amp./ft.² (1.08 amp./dm.²)

Composition of electrolyte: (g./l.)				Zinc content of deposit (per cent)	Cathode efficiency (per cent)
Tin	Zinc	Total cyanide	Sodium hydroxide		
5	1.0	20.1	2.5	—	38
10	1.0	20.1	2.5	7.2	72
20	1.0	21.6	2.5	7.3	92
30	1.0	22.6	2.5	6.6	99
50	1.0	20.2	2.5	7.4	98
30	1.8	22.5	3.6	14.0	—
30	2.0	22.0	5.0	15.8	90
30	2.5	24.5	4.3	22.0	—
30	3.0	24.5	5.0	24.6	91
30	3.6	28.0	4.8	30.0	—
30	8.0	41.0	5.0	47.0	—
30	12.0	53.0	12.5	72.0	—

tion, and a systematic investigation was consequently made of the influence of the several variables associated with the plating process on the composition of the alloy deposit and efficiency of deposition. Latterly, when it was found that more zinc was needed to confer maximum corrosion resistance, the work was extended to cover alloys of higher zinc content.

A résumé of the effect of variables was given in the original paper (1). The account which follows is an amplification and, in some instances, a modification of the earlier statements.

Influence of the metal content of the electrolyte

Other factors being constant, the composition of the cathode deposit is found to depend far more on the zinc content than on the tin content of the electrolyte. For a constant zinc content, an increase in the amount of tin in the bath from 10 g./l. to about 50 g./l. has little influence on the composition of the deposit. An increase in the zinc content of the bath, however, the tin being maintained constant, leads to a progressive increase in the amount of zinc in the deposit (Table I). The cathode efficiency increases as the tin concentration is increased and reaches a maximum at 30 g./l.

of tin. With higher concentrations of tin the efficiency remains substantially constant; there is, thus, no advantage in increasing the tin concentration beyond 30 g./l. and, on the contrary, higher concentrations tend to increase the loss of tin through dragout.[3] Additional results, not reported in Table I, for solutions of different concentration, indicate that the cathode efficiency increases progressively but slowly with increase in the zinc concentration of the bath.

As a result of these tests, a tin concentration of 30 g./l. and zinc concentrations of 2.5 g./l. and 8 g./l., respectively, were standardized for depositing 78 per cent tin and 50 per cent tin alloys.

Influence of total cyanide concentration

Throughout this report the figures quoted for total cyanide refer to the whole of the cyanide in the bath, expressed as sodium cyanide, and, thus, include the free sodium cyanide, the combined sodium cyanide, and the sodium cyanide equivalent of the cyanide in the $Zn(CN)_2$. This means of representation is practicable and convenient because the method of determining cyanide in these solutions developed by the Tin Research Institute and described in the earlier publication gives the sodium cyanide equivalent of all the CN groups in the bath.

As already pointed out, an increase in total cyanide at first rapidly reduces the amount of zinc in the deposit but, after a certain critical concentration has been reached, exerts little further influence on composition (Fig. 4). The inflexion in the curve occurs at a concentration of about 15 g./l. of *free* sodium cyanide and, over the range of alloys studied, this figure appears to be independent of the amount of zinc in the solution. The *total* cyanide content, as defined above for any bath, is equal to the free sodium cyanide content plus three times the zinc metal content.[4] Hence, the position of the inflexion in terms of total cyanide can readily be determined for any solution. To allow sufficient latitude in working, the minimum free sodium cyanide concentration has been fixed at 17.5 g./l.; experience has shown that maintaining the free cyanide at 17.5–20.0 g./l. gives satisfactory results from the viewpoints of control of the deposit and economy in the use of cyanide.

The curves reproduced in Fig. 4 have been derived by the above rule from a basic curve determined for the deposition of alloys containing 92 per cent of tin and from the results of extensive tests on the deposition of higher-zinc alloys from large baths, and are intended to serve as a guide to the control of the process. Provided the total cyanide concentration is not initially below the permissible minimum values indicated on the curves, which in each case correspond to 17.5 g./l. of free sodium cyanide, the bath can be operated for at least twenty-four hours without any risk of the cyanide concentration being reduced by hydrolytic decomposition to a dangerously low value.

[3] There is some evidence in the deposition of tin-copper alloys from sodium stannate-sodium cupro-cyanide solutions that the reduction in cathode efficiency, which normally results from accumulation of carbonate in used solutions, can be at least partly prevented by increasing the tin content of the bath beyond the value giving maximum efficiency in new, carbonate-free solutions. It is conceivable that tin-zinc solutions may behave similarly, and the matter is being investigated.

[4] $Zn(CN)_2 \cdot 2NaCN$ is estimated analytically as 4NaCN. $4NaCN = 4 \times 49 = 196$; $3Zn = 3 \times 65.4 \simeq 196$.

Variation in the cyanide concentration has no significant influence on cathode efficiency. No advantage is gained by keeping the amount of cyanide above the recommended operational value; on the contrary, an excessive increase in cyanide is likely to lead to a reduction in anode efficiency, as occurs with pure tin anodes in the deposition of tin-copper alloys from stannate-sodium cupro-cyanide solutions (6).

Influence of sodium hydroxide concentration

An increase in the sodium hydroxide content of the bath leads to a reduction in the tin content of the deposit, the relationship being approximately linear. Fig. 5 shows that the effects of a change in hydroxide concentration for solutions containing 30 g./l. of tin and, respectively, 1.0 g./l. and 2.5 g./l. of zinc are similar. The inference is, therefore, that the enrichment of the deposit in zinc resulting from an increase in hydroxide is due, not to the conditions having been made more favorable for the deposition of the zinc, but to the suppression of the deposition of the tin. For these solutions it would seem that an alteration in hydroxide concentration has, in fact, little or no direct effect on the deposition of the zinc. As would be anticipated, the suppression of the deposition of the tin is accompanied by a gradual fall in the cathode efficiency which diminishes from 95 to 96 per cent with less than 7.5 g./l. of hydroxide to a little over 80 per cent with 22.5 g./l. of hydroxide. Owing to this reduction in efficiency, it is not practicable to rely alone on the effect of a high content of hydroxide to suppress the tin when depositing alloys of high zinc content, and when depositing alloys containing more than about 25 per cent zinc it is, therefore, necessary also to increase the zinc content of the electrolyte.

Effect of temperature

As the working temperature of the bath is increased, the zinc content of the deposit slowly increases and reaches a maximum at about 70°C.; at 80°C., the amount of zinc in the deposit commences to diminish very rapidly, and at a slightly higher temperature for solutions containing 1 g./l. of zinc falls to less than 1 per cent. The cathode efficiency increases with temperature from a low value at 25°C. to approximately 100 per cent at 80°C. These observations apply in general to the whole range of tin-zinc electrolytes.

To insure a high efficiency, a high working temperature is thus essential. Although the composition of the deposit is not greatly affected by variation in temperature, the steepness of the cathode efficiency-temperature curve demands that the temperature be fairly closely controlled. The working temperature was originally fixed at 70° ± 2°C., but this figure has now been reduced to 65° ± 2°C. The rate of decomposition of cyanide increases very rapidly as the temperature is raised above 65°C., and the slight fall in efficiency resulting from a reduction of 5°C. in the working temperature is more than compensated by the saving in cyanide.

Control of the temperature within a range of 4°C. does not appear to present any practical difficulties. At 65° ± 2°C. and with appropriate current densities, a cathode efficiency of over 90 per cent is attainable for the entire range of tin-zinc plating solutions.

Cathode current density

The figures in Table II show that the cathode current density can be varied over a wide range without seriously altering the composition of the deposit. However, the effect of a change in current density on the cathode efficiency must also be considered. With solutions containing 2.5 g./l. or more of zinc, the efficiency remains above 90 per cent up to a current density which increases with the zinc content of the bath and which is at least 20 amp./ft.^{2} (2.15 amp./dm.^{2}) for still solutions. When depositing high-tin alloys from solutions containing only 1 g./l. of zinc, on the other hand, the cathode efficiency changes so rapidly with current density that fairly close control of the latter becomes essential.

TABLE II. *Influence of cathode current density on the composition of the deposit and efficiency of deposition*

Temperature: 70°C.

Composition of electrolyte: (g./l.)				Cathode current density		Zinc content of deposit (per cent)	Cathode efficiency (per cent)
Tin	Zinc	Total cyanide	Sodium hydroxide	amp./ft.^{2}	amp./dm.^{2}		
30	1.0	18.0	2.5	2.5	0.27	—	110*
30	1.0	18.6	2.5	5	0.54	0.1	110*
30	1.0	18.0	2.5	10	1.08	—	99
30	1.0	20.1	2.5	15	1.62	9.4	83
30	1.0	19.5	2.5	15	1.62	8.2	82†
30	1.0	18.0	2.5	20	2.16	—	43
30	1.0	20.1	2.5	20	2.16	9.7	42
30	1.0	19.6	2.5	30	3.24	6.1	16
30	2.8	24.6	4.3	5	0.54	13.6	96
30	2.8	24.6	4.3	10	1.08	19.9	98
30	2.8	24.6	4.3	15	1.62	22.7	93
30	2.8	24.6	4.3	20	2.16	24.2	91
30	2.8	24.6	4.3	30	3.24	21.2	76
30	2.8	24.6	4.3	40	4.32	17.8	67

* Bivalent tin present in solution.
† Temperature: 75°C.

The normal cathode current density range for still tin-zinc solutions is 10–30 amp./ft.^{2} (1.08–3.24 amp./dm.^{2}). It is possible that the upper current density limit might be extended and a high efficiency still maintained by movement of the work during plating. Reference is made later to a semi-automatic, tin-zinc plating plant with moving cathodes, but as this plant has only recently been installed the effect of cathode movement has not yet been fully investigated.

Cathodic polarization and throwing power

Using a cell of 500 ml. capacity equipped with concentric electrodes, a study was made of the effect of cathode current density on cathode potential for tin-zinc solutions of various zinc contents and for a sodium stannate tin-plating solution, the tin content in all cases being 30 g./l. Fig. 6 summarizes the results of these tests. Addition of zinc to a straight stannate solution ennobles the cathode potential at all current densities above 0.5

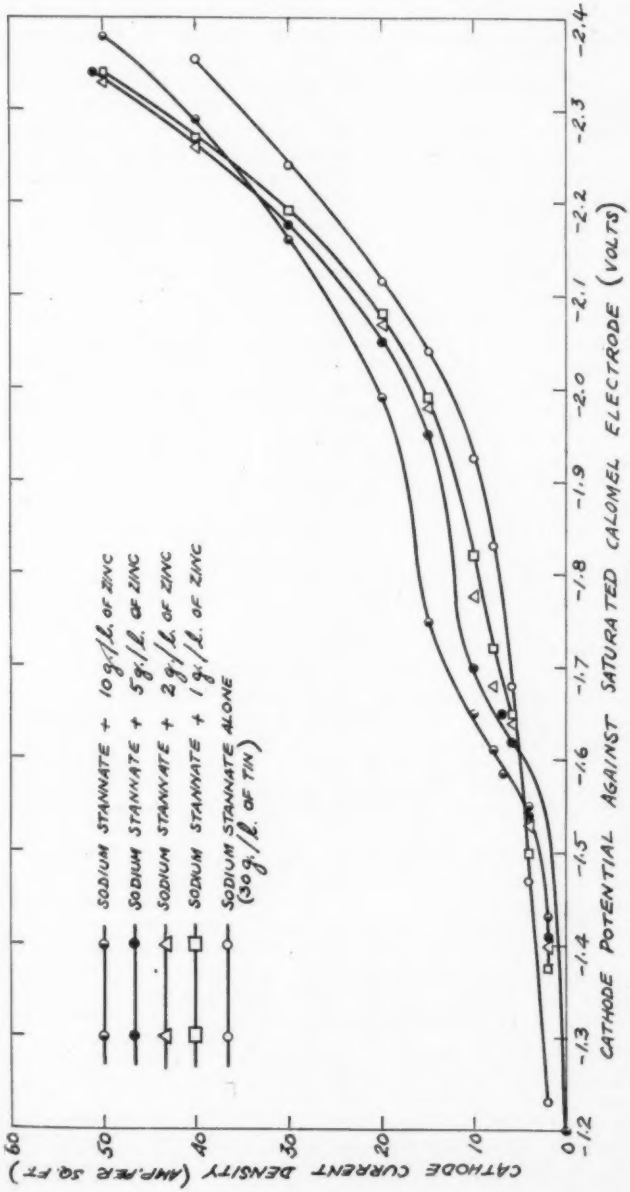
CATHODE CURRENT DENSITY (AMP. PER SQ. FT.)
0
10
20
30
40
50
60
-1.2
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
-2.1
-2.2
-2.3
-2.4
CATHODE POTENTIAL AGAINST SATURATED CALOMEL ELECTRODE (VOLTS)
SODIUM STANNATE + 10 g./L. OF ZINC
SODIUM STANNATE + 5 g./L. OF ZINC
SODIUM STANNATE + 2 g./L. OF ZINC
SODIUM STANNATE + 1 g./L. OF ZINC
SODIUM STANNATE ALONE (30 g./L. OF TIN)

FIG. 6

amp./ft.^{2} (0.054 amp./dm.^{2}) to an extent depending on the current density and amount of zinc present. The greatest change in cathode potential with current density occurs over a range of approximately 6 amp./ft.^{2} to 30 amp./ft.^{2} (0.64 to 3.24 amp./dm.^{2}) and this range embraces the practical current density limits. Over this range, all of these solutions are typified by high throwing power. No actual determinations of throwing power outside these limits have been made, but at lower and, to a less extent, at higher current densities, the deposit becomes enriched in tin and, consequently, the throwing power of the bath at these extremes, considered from the composition rather than from the thickness aspect, is low. This effect is much more noticeable at very low than at very high current densities and, therefore, when plating recessed articles, it is advisable to adjust the average current density so that it is nearer to the maximum than to the minimum value of the working range. There is, then, less likelihood of the minimum current density on the remote parts of the cathode falling to the danger point where the throwing power of the zinc is impaired.

Experimental determination of the throwing power of an alloy plating bath involves not only measurement of the thickness or weight of the deposit on selected parts of the cathode surface but also an estimation of any accompanying changes in its composition. The throwing power of the 80 per cent tin alloy has been determined by analysing the deposits on sheet steel cathodes bent at a right angle in the center and plated: (a) with one surface vertical and the other horizontal and facing the anode, and (b) with the two arms of the angle section running vertically, the apex of the angle directed away from the anode (Fig. 7 and 8). After plating at a current density of 15 amp. /ft.^{2} (1.62 amp./dm.^{2}) to a nominal thickness of 0.0005 in., the sheets were flattened out and cut into strips parallel to the bend as shown, and the thickness and composition of the deposit on each strip was determined. For purposes of comparison, similar strips were plated with cadmium and the thickness distribution determined.

The curves show the results obtained. Considering first the more drastic tests on the larger cathodes (Fig. 7), the thickness of the tin-zinc deposit diminishes from 0.00055 in. at the top of the vertical portion to 0.00035 in. at the bend; on the horizontal portion the thickness then increases again reaching 0.00058 in. at 1 in. from the end. Within the last 1 in. the thickness increases very rapidly to 0.00083 in. owing to the close proximity of the edge of the sheet to the anode. The composition of the deposit on both parts of the cathode remains approximately constant at 80 per cent of tin to within about 1 in. of the bend where the tin content increases to 90 per cent. Considering the severity of the test these results are encouraging. The curve for the thickness distribution of cadmium on a similar cathode is not directly comparable with the tin-zinc curve, as the average thickness of the cadmium is only about half that of the tin-zinc. The preparation of the cadmium plated samples for these tests was entrusted to an outside firm, and a thickness of 0.0005 in. was specified.

Turning to the tests on the smaller cathodes (Fig. 8), the thickness of the tin-zinc plate falls from 0.0007 in. at the edge to 0.00052 in. at the bend while the composition nowhere varies by more than 2.5 per cent. The fall in thickness is greater for the cadmium plate which diminishes from 0.00069 in. at the edge to 0.00041 in. at the bend. The excellent throwing

power of the tin-zinc plate, as revealed by this test, has been fully substantiated by corrosion tests; no marked falling off in protection in the

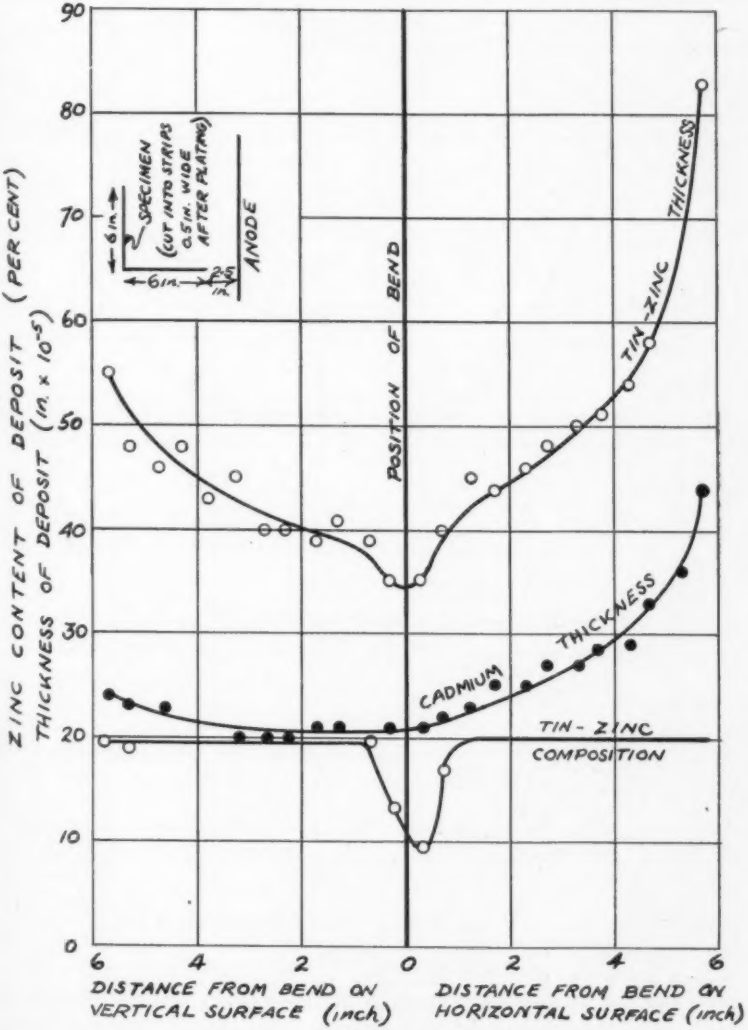

FIG. 7

corners and angles of radio chassis and similar articles plated with tin-zinc has been detected.

For the bulk of work for which tin-zinc plate is suitable it is not necessary to employ internal anodes to secure adequate uniformity of thickness and composition. With very deeply recessed articles, however, such as

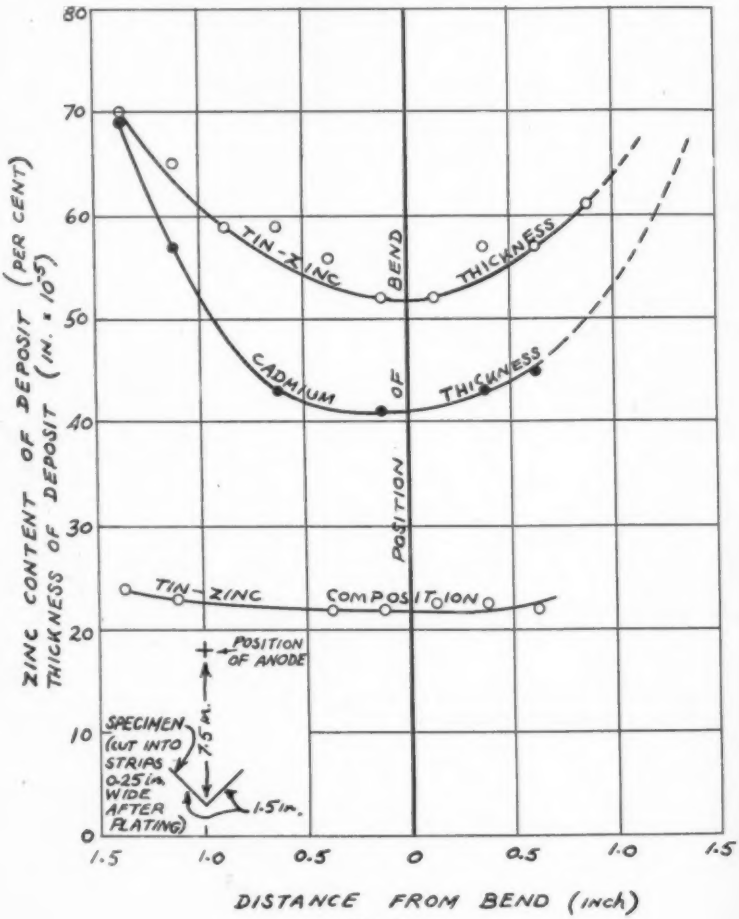

FIG. 8

normally call for the use of internal anodes, plating with external anodes alone may not prevent the zinc content of the deposit at remote points falling to a low value. In extreme cases, although the deposit may everywhere be thick enough, the composition in shielded angles and crevices may approach 100 per cent tin. The co-deposition of even a very small amount

of zinc with the tin improves protective value on account of the resulting reduction in the porosity of the tin.

ANODIC REPLENISHMENT OF THE BATH

Alloy anodes of the same composition as the plate to be deposited are used in tin-zinc plating. To insure the tin dissolving wholly in the quadrivalent form, the anodes must be operated in a filmed condition. The film is established exactly as in tin plating practice and, for alloy anodes containing up to 30 per cent zinc, is equally as easy to maintain during working. When the zinc content is increased to 50 per cent or more, the maintenance of the film becomes progressively less easy, partly because the

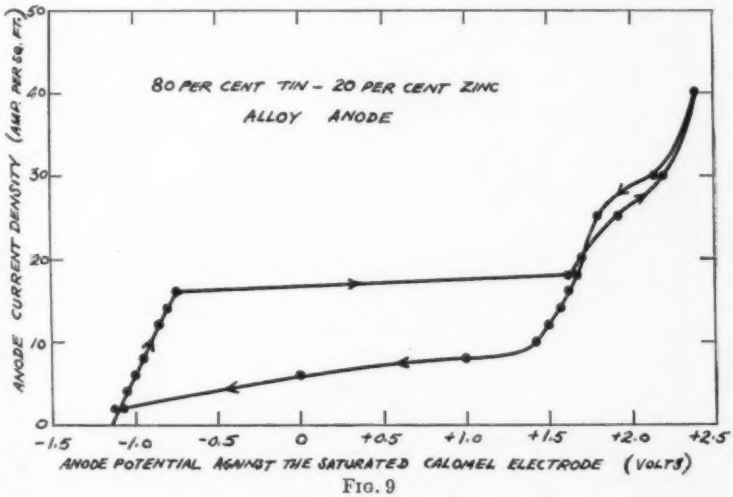

FIG. 9

permissible anode current density range grows more restricted and partly owing to mechanical weakening of the film resulting from the diminishing percentage of tin at the anode surface, as a result of which the film becomes more susceptible to the disruptive influence of impurities in the electrolyte.

Using the cell previously employed for studying cathodic polarization, the influence of the anode current density on anode potential for 80 per cent tin and 50 per cent tin anodes has been investigated. The results obtained for the respective alloys are shown in Fig. 9 and 10. Considering first the 80 per cent tin anode, starting with an unfilmed anode the current density increases almost linearly as the anode potential is increased. The linear relationship terminates abruptly at a current density of 16 amp./ft.^{2} (1.72 amp./dm.^{2}) when there is an increase of more than 2 volts in the potential of the anode resulting from the establishment of the anode film. Below 16 amp./ft.^{2}, the tin in the anode dissolves entirely in the bivalent form at an efficiency approaching 100 per cent. The current density corresponding to the completion of the filming process is about 18 amp./ft.^{2}

(1.94 amp./dm.^{2}). When the filming is complete, the tin dissolves in the quadrivalent form and continues to do so at a diminishing efficiency as the anode potential, and hence the anode current density, is further increased. Beyond 18 amp./ft.^{2} the anode potential-current density relationship is at first approximately linear, but the potential soon increases more rapidly than the current density, and ultimately the anode becomes completely passive. The onset of passivity is not clearly marked either in these experiments or in actual plating practice. Passivity is certainly incipient, however, at a current density not far removed from that corresponding to the completion of the anode film.

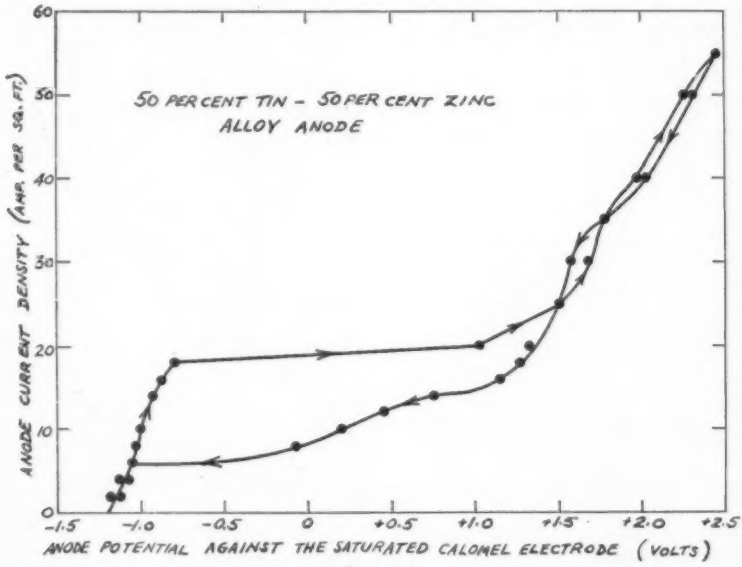

FIG. 10

On reducing the anode potential from the maximum value recorded, the curve at first retraces itself, but there is a hysteresis effect commencing at the point where the formation of the film was complete. A linear relationship between anode potential and current density persists well beyond this point, and there is no indication of disappearance of the film until the potential has fallen to a value corresponding to a current density of 10 amp./ft.^{2}(1.08 amp./dm.^{2}). Thereafter, the potential falls rapidly until the two curves converge at a current density of 4 amp./ft.^{2} (0.43 amp./dm.^{2}). The film has now completely disappeared, and the tin in the anode again dissolves in the bivalent form. It is thus evidence that in order to keep the anode properly filmed, and at the same time guard against any tendency towards passivity, the current density must be within the range of 10–18 amp./ft.^{2} (1.08–1.94 amp./dm.^{2}). Practical experience with cast anodes

in large baths indicates that these limits are a little on the high side and for new solutions the optimum range is 7.5–15 amp./ft.^{2} (0.81–1.62 amp./dm.^{2}).

Turning to the 50 per cent tin alloy, the onset of film formation is now delayed to a current density of 18 amp./ft.^{2}, and the potential increase during filming is smaller than for the 80 per cent tin alloy. On increasing the potential after filming is complete, the anode rapidly becomes passive, at least in so far as its tin content is concerned. Passivity again increases progressively, and its onset is even less clearly defined than in the preceding case; the departure in this respect from the usual form of polarization curve for a pure metal and its accentuation with 50 per cent of tin as compared with 80 per cent of tin is attributed to the presence of the two metals in the anodes. When the potential is reduced, the film begins to disappear at a current density of about 16 amp./ft.^{2} (1.72 amp./dm.^{2}). Compared with the 80 per cent tin anode, the filming current density range is, thus, considerably narrower while the upper and lower current density limits are higher. The working current density range is further restricted by the more rapid onset of passivity.

The efficiency of dissolution of tin-zinc alloy in these solutions diminishes as the anode current density is increased. A revised efficiency curve for the 80 per cent tin alloy together with a curve for pure zinc are reproduced in Fig. 11, and it is seen that the efficiency of the alloy anode falls very rapidly when the current density exceeds 20 amp. /ft.^{2} (2.16 amp./dm.^{2}). This result has already been predicted from the polarization curve. At 69 amp./ft.^{2} (6.48 amp./dm.^{2}), the anode efficiency is only a little over 10 per cent; complete passivity does not develop, however, until a considerably higher current density is reached. If there is any iron in the solution passivity is facilitated, and the current density corresponding to complete passivation is reduced by an amount which may be substantial if much iron is present.

It will be noted that the anode efficiency of pure zinc in the tin-zinc electrolyte is very low, even at low current densities; alloying with tin raises the efficiency and in practice no difficulty is experienced in replenishing and in maintaining the zinc content of the bath anodically.

PRACTICAL EXPERIENCE IN THE ELECTRODEPOSITION OF TIN-ZINC ALLOYS

The bath compositions which have been standardized for depositing the 80 per cent tin and the 50 per cent tin alloys respectively are given in Table III.

An 80-gallon bath and a 200-gallon bath depositing the 80 per cent tin alloy and the 50 per cent tin alloy respectively have been in use in the laboratory for several years. A large volume of work has been put through these two baths and much valuable information has been gained from a study of their performance.

After the first announcement of tin-zinc plating, a few industrial concerns installed experimental plants, but although satisfactory results were reported, the new protective finish has only recently been developed on an industrial scale. Some three months ago a large firm manufacturing electrical components in Great Britain decided to try out tin-zinc as an alternative to electrodeposited cadmium and converted a 750-gallon cadmium-plating bath to deposit tin-zinc (80 per cent tin). As a result of experience

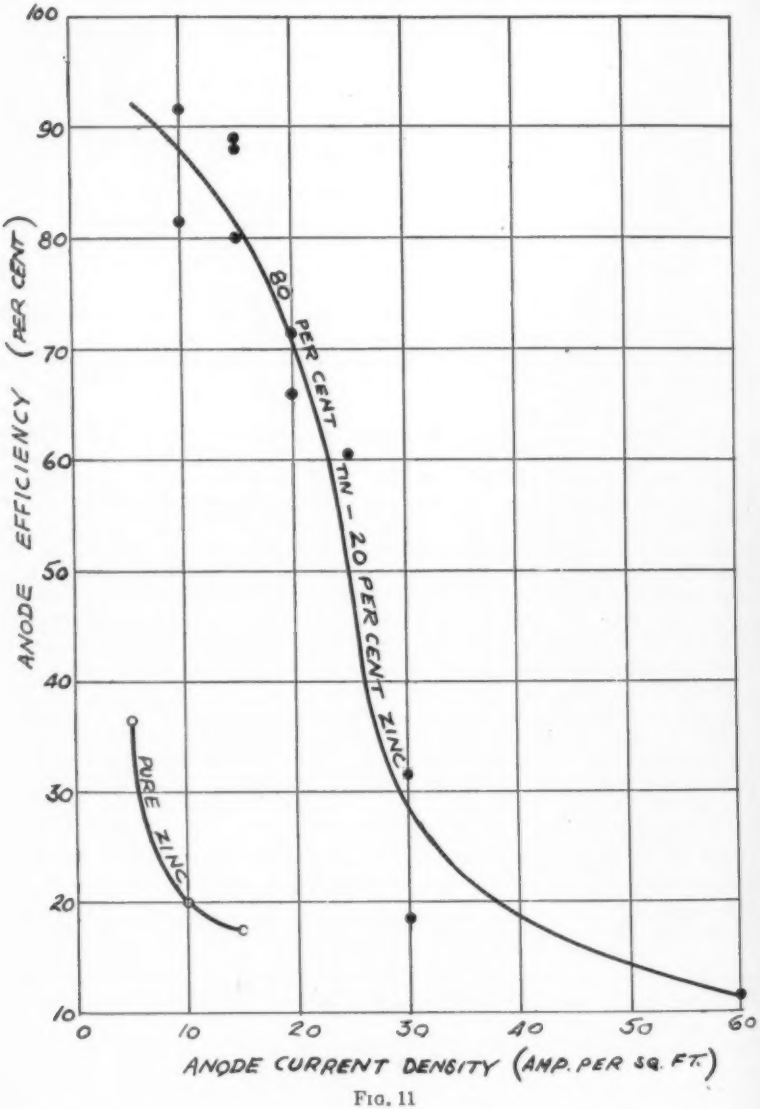

FIG. 11

with this bath, this firm has now converted two further baths of the semi-automatic type, of 750- and 1250-gallons capacity respectively, from cadmium to tin-zinc, and the conversion of a fourth bath is contemplated. The 1250-gallon bath is featured in Fig. 12.

Plating tanks. Effect of iron in the electrolyte

Up to the present time plating tanks have been of welded steel with the sides protected by detachable sheets of reinforced glass. This type of tank has proved to be unsuitable for depositing the 50 per cent tin alloy.

TABLE III. *Chemical constitution of tin-zinc alloy plating solutions*

Constituent	For depositing 80 per cent tin alloys		For depositing 50 per cent tin alloys	
	(g./l.)	(oz./U. S. gal.)	(g./l.)	(oz./U. S. gal.)
Tin	30	4.0	30	4.0
Zinc	2.5	0.3	8	1.1
Sodium hydroxide	4–6	0.5–0.8	6–8	0.8–1.1
Total cyanide*	25–28	3.3–3.7	52–55	6.9–7.3
Free sodium cyanide	17.5	2.3	17.5	2.3

* Expressed as sodium cyanide.

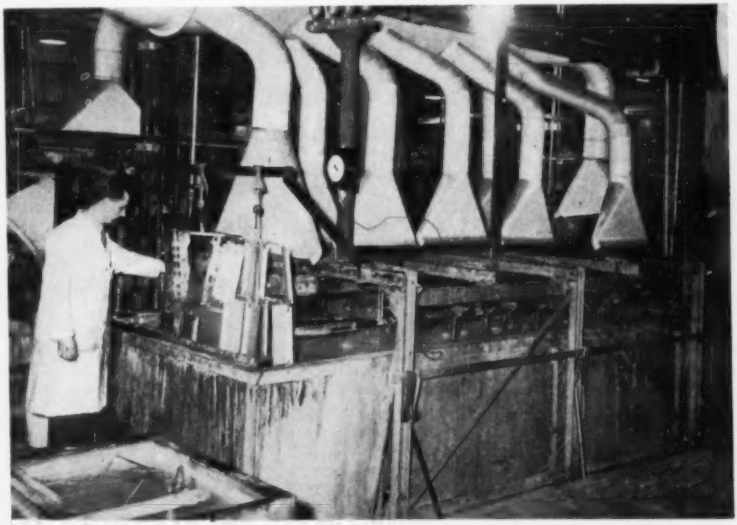

FIG. 12. 1250 gallon semi-automatic tin-zinc plating installation. Courtesy of Messrs. E. M. I. Factories, Ltd.

When freshly made up, a 50 per cent tin alloy plating bath contained in an iron tank works quite satisfactorily and there is no difficulty over anodic replenishment, despite the aforementioned narrow anode current density range. After some time in use, however, the anodes begin to give trouble. A tenacious deposit forms on their surface hindering dissolution and eventually making it impossible to keep the anodes properly filmed; as a result, bivalent tin enters the solution and ruins the cathode deposit.

Moreover, solid particles tend to become detached from the anode surface and migrate to the cathode where they cause roughening of the work. These troubles have been traced to the effect of iron which accumulates in the solution through chemical attack of the exposed iron of the tank by the hot cyanide. The iron is initially present as sodium ferrocyanide, and this compound reacts with the zinc in the anode to form insoluble zinc ferrocyanide which is responsible for the anodic deposit and contamination of the cathodes. In lesser degree, this trouble occurs in brass plating practice. Continuous filtration of the bath will prevent the roughening of the cathodes but cannot improve the anodic conditions and, as there is no known method of removing the ferrocyanide by direct chemical precipitation, the only expedient with contaminated solutions is to operate them with insoluble anodes. The 200-gallon bath referred to above has in fact been operated in this way for some considerable time, the tin and zinc being added to the solution as required and perfectly satisfactory plate has been obtained, but the resulting enrichment of the bath in hydroxide is an objection.

Anodic replenishment when plating high-zinc alloys is, thus, only practicable with iron-free solutions and a lined tank must therefore be employed. Few materials will withstand the combined effects of high temperature, sodium hydroxide, and sodium cyanide, but some forms of rubber are claimed to do so. A rubber-lined electrically-heated tank has recently been installed for experimental purposes, but no data on its performance are as yet at hand.

While the 80 per cent tin plating solutions similarly attack iron, the iron appears to be far less harmful than with the higher-zinc alloy. Glass-lined iron tanks have been employed in the laboratory and are in use in the industrial plant just mentioned and, so far, have given no serious trouble with this solution. Nevertheless, pending further experience on a long term production basis, it cannot be assumed that this freedom from trouble will be permanent, and ultimately it may transpire that a completely protected tank is necessary to insure a long service life from the bath. Roughening of the work through zinc ferrocyanide contamination has never been observed, while quite large amounts of iron in solution can be tolerated without interfering with the anode process. After three months in use, the 750-gallon bath mentioned above had an iron content of 1.9 g./l. and was working quite satisfactorily. The most noticeable effect of iron in the high-tin alloy bath is an increased tendency for the anodes to become passive at the upper end of the normal anode current density range. It is necessary to reduce the maximum current density as the iron content of the bath increases, but there is considerable latitude before the current density has to be lowered to a point where the stability of the anode film is endangered. During the three months that it has been in use the 750-gallon bath has been operated at 70°C. A reduction of the working temperature to 65°C., as has since been deemed desirable for other reasons, will, it is thought, slow up the rate of attack of the iron.

Maintenance of the 80 per cent tin alloy bath

With properly adjusted working conditions, there is not much change in the tin and zinc contents of the bath over long periods of time. The sodium

hydroxide diminishes slowly and the sodium cyanide more rapidly in use so it is advisable to check the amounts of these constituents daily. An increase in the working temperature above 65°C. has little influence on the rate of loss of hydroxide but greatly increases the rate of decomposition of the cyanide. When working at the originally recommended temperature of 70°C., the consumption of cyanide in an aggregate of 2000 gallons of solution was around 100 lb. per 24-hour day. Lowering the temperature to 65°C. reduced this figure by more than 50 per cent. These observations relate to comparatively new solutions, and experience indicates that the cyanide consumption tends to diminish as the solution ages.

The figures in the following table for three week's operation of a 750-gallon, still bath give some idea of the consumption of the constituents of the electrolyte under industrial conditions. This bath has been in use, on

TABLE IV. *Chemical control figures for 750-gallon, tin-zinc bath, operated at 70°C.*
Average composition of deposit: 78 per cent tin-22 per cent zinc

Date	Composition of solution: (g./l.)				Additions: (kg.)			
	Tin	Zinc	Sodium hydroxide	Total cyanide	Sodium stannate	Zinc cyanide	Sodium hydroxide	Sodium cyanide
12/29/47	29.6	2.40	4.6	26.7	(First date on full production)			
2/17/48	28.6	2.40	4.8	25.4	11.3	0.6	2.4	11.5
2/18/48			5.3	26.9			0.6	6.8
2/19/48	29.3	2.50	5.3	25.5	5.7		0.6	11.3
2/20/48			5.4	25.5				11.3
2/23/48			4.6	27.0			3.4	6.0
2/24/48	29.6	2.46	5.0	26.9			1.6	6.6
2/25/48			5.2	27.0				6.0
2/26/48	29.5	2.49	5.1	27.8			1.3	3.4
2/27/48			5.1	25.5			3.1	11.3
3/ 1/48	27.7	2.46	5.1	25.5	19.0	0.2	1.3	11.4
3/ 2/48			5.4	25.9			0.5	10.0
3/ 3/48	28.7	2.41	5.1	25.5	10.5	0.6	1.3	11.4
3/ 4/48			5.3	25.5			1.1	11.5
3/ 5/48			5.4	23.8			2.3	18.2

an average, for 100 hours per week. It is emphasized that the temperature of the bath throughout has been maintained around 70°C. As there was no thermostatic control, higher temperatures may often have been reached, which would help to account for the erratic variations in the consumption of cyanide. It is intended to reduce the temperature of this bath to 65°C. and to install automatic temperature control. These changes should substantially reduce the cyanide consumption.

Anodes

Cast anodes are quite satisfactory and should be of the same composition as the alloy being deposited. An oval section is favored, but flat anodes may be used provided they do not exceed about 4 in. in width. Anodes should have cast-in or screwed-in connectors which should be of steel if there is any possibility of their being immersed in the solution. The anodes must be firmly in contact with the electrical supply, for example by clamping the hooks to the anode bars with a quick release device. A

single, bad anode contact is sufficient to cause rapid contamination of the bath by bivalent tin.

The anodes must at all times be operated in a filmed condition. In large installations the most convenient way of establishing the film is by raising the bath voltage for 15–30 seconds to about 2 v. above the normal working value, usually 3.5–4.5 v. There is no objection to loading up the bath with unfilmed anodes provided not many minutes elapse before the filming voltage is applied. Zinc tends to reduce quadrivalent tin, and, hence, the anode conditions are more exacting than in stannate tin plating where filmed anodes can safely be left in the bath for a considerable time with no current flowing. However, tin-zinc anodes containing 80 per cent tin retain their film long enough to allow them to be left quiescent in the bath for at least two hours. The film is lost at an increasing rate as the zinc content of the anodes is increased, and high-zinc anodes cannot, therefore, be left in the solution for so long in an inactive state.

When plating the interior of cylindrical articles, it is sometimes impossible to provide sufficient anode area in the space available. Under these conditions, it is necessary to resort to the use of insoluble anodes. Some success has been obtained in the depositing of tin-zinc plate on the interior of fire extinguisher bodies using iron anodes. Resorting to such subterfuges as corrugated or composite anodes to increase the effective anode area is neither recommended nor practicable, as the anodes tend to become passive on the high current density areas and to lose their film on the low current density areas.

PASSIVATION OF TIN-ZINC PLATE

Tin-zinc plate of any composition can be passivated and its already excellent resistance to corrosion further increased by treatment in hot, 2 per cent chromic acid solution. The thickness of the passive film and depth of coloration increase with the time of immersion and, more particularly, with the temperature of treatment. Treatment for 30 seconds at 80°C. produces a yellow or brown film; immersion for 15 seconds at 50°C. gives a thin, colorless film. From the corrosion viewpoint, it is not usually necessary to passivate tin-zinc plate, but the chemical surface treatment has the advantage of reducing any tendency of the plate toward finger-marking. The lower-temperature treatment is generally preferred as it preserves the appearance of the plate and does not impair its solderability.

PROPERTIES AND USES OF ELECTRODEPOSITED TIN-ZINC ALLOYS

A report on the corrosion-resisting properties of these alloys has been published elsewhere (7). Humidity, salt-spray, hot-water porosity, and outdoor exposure tests have been carried out on steel specimens coated with tin-zinc deposits of various compositions and thicknesses. In every case, the optimum tin content has proved to be 75–80 per cent. With more tin, the deposits tend to resemble electrodeposited tin but are less porous, whereas with less than 50 per cent tin they become more like zinc in character. From 80 per cent down to 50 per cent tin, the corrosion resistance falls slowly but is still fairly high for the lower-tin alloy. Solderability, which is excellent for the 80 per cent tin alloy, deteriorates steadily with reduction in tin content.

Irrespective of composition, the recommended thickness of tin-zinc plate for most applications is 0.0005 in. Under particularly severe conditions, especially with the lower-tin alloys, the thickness can, with advantage, be increased to 0.001 in. The minimum thickness should not be less than about 0.0003 in. as thinner deposits are liable to be porous.

The electrode potential of high-tin, tin-zinc alloys in salt solutions appears to be close to the potential of zinc. Tests were made on tin-zinc, tin, and zinc deposits, 0.005 in. thick, immersed in potassium chloride solution for fifteen days, with the results shown in Table V.

Tin and zinc form a simple eutectiferous series, the eutectic containing 92 per cent tin (8); the 78 per cent tin alloy, therefore, contains free zinc which, being electrochemically the more reactive metal, determines the potential of the alloy. As would be expected, the potential of the 50 per cent tin alloy is almost the same as that of the 78 per cent tin alloy.

The hardness of tin-zinc plate containing 80 per cent tin is 37 on the Vickers scale. The hardness of cast tin-zinc of this composition is about 18, and the greater hardness of the electrodeposited alloy is attributed mainly to its much finer structure. Tin-zinc plate is extremely ductile and

TABLE V. *Electrode potentials against the saturated calomel electrode*

Aerated 3 per cent potassium chloride solution. 25° ± 0.1°C.

Electrode	Electrode potential:	
	At commencement	After 15 days
	volts	*volts*
78 per cent tin-22 per cent zinc	−1.0	−0.99
Zinc	−1.03	−1.03
Tin	−0.45	−0.44

mechanical deformation of tin-zinc plated steel, for example by bending does not rupture the coating or seriously reduce its protective value. Being harder than tin, the alloy plate can be readily polished to a brilliant luster.

So far, the electrical industry has been the chief user of tin-zinc plate, and is turning to the 80 per cent tin alloy as an alternative to cadmium for the protection of radio chassis, loudspeaker frames, valve screens, and other components. Since the plate stands up well to marine atmospheres, it is attracting some interest for the protection of ship's fittings, etc. There are many further applications in engineering where, it is thought, the new finish will find an outlet. Tin-zinc coated steel may prove useful for the manufacture of certain containers, e.g., for sifting talcum powder where, owing to the service conditions, thinly coated electro-tinplate does not always give entirely satisfactory results. For general out-of-doors protection of structural steel, the 50 per cent tin alloy appeals on economic grounds, but, owing to the technical difficulties mentioned earlier, it is considered that hot-dipping rather than electrodeposition may prove to be a more suitable method of applying alloys of this composition to steel.

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Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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EFFECTS OF OPERATION ON ELECTRIC FURNACE REFRACTORIES[1]

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ABSTRACT

A general discussion is presented covering the refractories used in basic and acid-type furnaces and in ladles. Refractory practices for furnaces and ladles are discussed from an operational viewpoint. Tjemmes states that longer refractory life can be obtained by better control over scrap charging methods, speed of melting, construction of masonry, and better utilization of the operator's skill. The refractory problem is more severe in furnaces making stainless steel owing to the severe oxidizing conditions. In this practice, it is indicated that the use of oxygen instead of "oreing down" decreases refractory costs.

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